Measurement of Particles in Liquid Materials Using the Light Scattering Method

Kaoru Kondo, Masaki Shimmura, and Takuya Tabuchi
Rion Co., Ltd.

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1. Background

A particle counter that measures the particles floating in a gas phase or liquid phase directly in a floating state using a light-scattering phenomenon has been widely used at the manufacturing site of various industries requiring cleanliness, as it can easily obtain detection sensitivity comparable with other methods and get measurement results immediately and continuously.

For the light-scattering phenomenon of particles, an exact solution was obtained at the beginning of the 20th century by G. Mie. After that, many numerical solutions[1)] have been studied. Mie's light-scattering theory has been recognized as the basic principle of equipment that measures the size or number of floating particles or surface particles because it can properly explain the light-scattering phenomenon of one particle and perform a quantitative analysis. On the other hand, Einstein, Debye, or Lorentz studied the light-scattering phenomenon of liquid as a method to obtain the behavior or physical properties of liquid molecules or polymers and systemized it gradually.[2)]

In the manufacturing process of a state-of-the-art semiconductor device, smaller particles must be detected to control contamination particles. In particular, it is remarkably required to control the particle contamination in liquid materials used in a wet process such as cleaning or lithography. At present, liquid-borne particles are mainly measured and controlled using a liquid-borne particle counter based on a light-scattering method. For the light-scattering behavior of particles, the intensity of scattered light rapidly decreases when the size of the particles becomes much smaller than its wavelength. Therefore, the detection technology of extremely weak light is used as a key technology to detect ultrafine particles using a light-scattering phenomenon. When a particle of several 10 nm in size is detected, the light-scattering phenomenon of the liquid that is the medium is found to be a significant influence on particle-sensing signals.

By showing the relative relation between the light-scattering phenomenon of particles and the light-scattering phenomenon by liquid, this paper provides a theme on the detection of ultrafine particles in liquid and describes particle detection technology, in which a multi-channel photo-detector intended for particle measurement in the polymer solution such as a photoresist, is used, as one of the methods to extract the scattered light of particles from the scattered light by liquid.

2. Light-scattering phenomenon of particles

In Mie's light-scattering theory, the spherical wave occurring when particles are polarized by the electric field of light under conditions in which an object (i.e., a particle) with a dielectric constant that differs from a peripheral one in finite size exists in the propagation area of light and when a dipole is vibrated in the size depending on the dielectric constant is prescribed as scattered light by particles. Since the second power of a refractive index is a dielectric constant, the size of scattered light depends on the refractive index of the particles or media. The scattering cross-section, which is the ratio of the scattered-light intensity in all directions, obtained by Mie's theoretical expression, to the light intensity irradiated on the projected cross-section of particles is shown in Figure 1. When particles and the irradiated light wavelength are approximate in size, the light-scattering intensity by the particles indicates complicated light-scattering characteristics without simply increasing according to the particle size. The scattering-cross-section is converged to 2 when particles are much larger than the wavelength of the irradiated light. When particle size becomes much smaller than the wavelength, the scattering-cross-section is proportional to the fourth power of the particle size. In this area, the dipole to be vibrated can be considered as one. Therefore, Mie's theory matches with the light-scattering expression of Rayleigh shown in expression (1). The light-scattering intensity (I_R) by particles is proportional to the sixth power of the particle size and is inversely proportional to the fourth power of its wavelength.

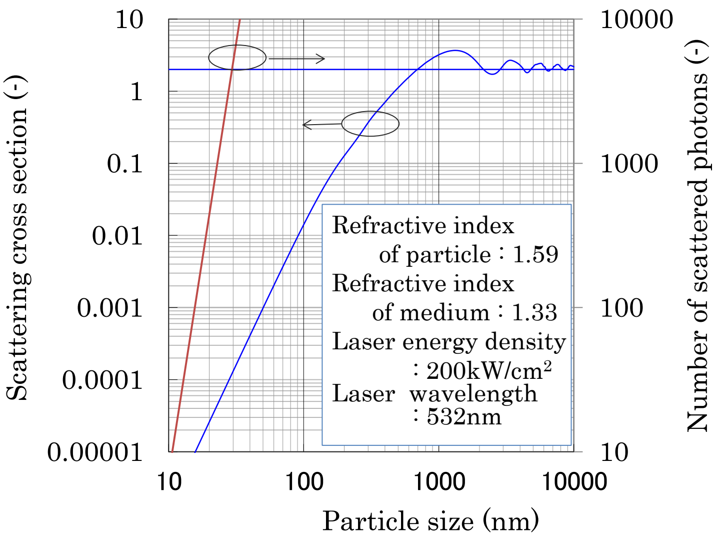


Fig.1 The scattering cross section of PSL particle in UPW.

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

Where, I_0 is irradiated light intensity, d is particle size, R is the distance between a measurement target and the measurement point, 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 light-scattering cross-section of particles with a size of 50 nm is approximately 0.001. As given in expression (1), in other words, the light irradiated on the projected cross-section of particles contributes to about 0.1% of the light scattering.. For a particle of 20 nm in size, light contributes to light scattering by only about 0.002%. The value, obtained when scattered light occurring in the case in which particles pass through a particle detection area (cross-section: approximately 10 μm × 25 μm) of 200 kW/cm^2 (wavelength 532 nm) in light energy density at a rate of 0.1 msec is converted into the number of photons, is shown in Figure 1. The number of photons is approximately 5,000 (5 pA) for a particle of 30 nm in size and approximately 400 (0.4 pA) for a particle of 20 nm in size. The scattered light of ultrafine particles is very low in light intensity. To detect the scattered light, it may also be required to process a discrete photon-sensing signal.

To confirm the consistency of the theoretical value and measured value of light scattering, the relative light-scattering behavior relation between the PSL (Polystyrene Latex) particles and Au particles dispersed in UPW (Ultra Pure Water) is shown in Figure 2. The complex refractive index of the Au particles was supposed to be 0.467-*i*2.41 (*i* is a complex number).[3] The calculated value is obtained from Mie's theoretical expression.[1] For the measured value, the median in the crest value distribution of a particle-sensing signal is used as the representative value of the particles. The calculated and measured values were made to coincide in a PSL particle of 55 nm in size. The PSL particle size is determined by the AIST (National Institute of Advanced Industrial Science and Technology).[4] For the Au particles, the evaluated value of particle size is reported by NIST (National Institute of Standards and Technology).[5] The measured value of particles is considered to completely coincide with the calculated value. It is found that the particle size of the Au particles, which is determined from the PSL particles used to indicate the scattered-light intensity, is within 3 to 4% of the geometric size.

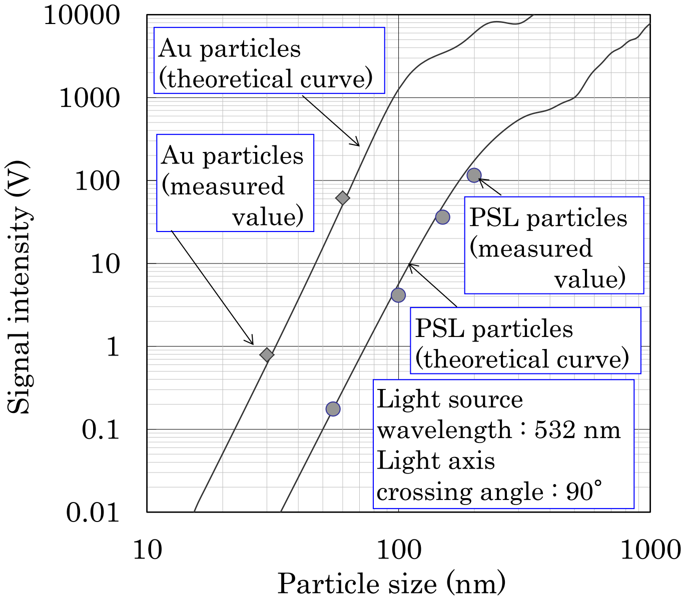


Fig.2 Correlation of light scattering characteristic of Au particle and PSL particle.

3. Light-scattering phenomenon of liquid

A particle counter separates scattering-light of particls, which particles passing through a particle detection area at random are scattered, from background light and recognizes it as a particle signal. With the appearance of fine particles to be detected, a medium (liquid, in this paper) that could be considered to be transparent until now significantly behaves as a scatterer and may cause an influence when detecting the particle signal. In other words, improving only a method to detect an extremely weak light signal suggests the possibility that the detection size of particles in liquid cannot be made finer.

In ideal pure liquid, in which the dielectric constant is completely uniform, any light-scattering phenomenon does not theoretically occur. In a weak light detection system corresponding to the light-scattering phenomenon of particles with a size of about 50 nm, however, the behavior of the background light (stray light) caused by the light-scattering phenomenon depending on the liquid itself has a significant value. The light scattering in pure liquid becomes slightly heterogeneous in density distribution due to the fluctuation of liquid molecules because the boundary surface of a minute dielectric constant exists (scattered points are localized). The scattered-light intensity (I_E) of liquid is obtained by the idea of Einstein's light scattering by molecular density fluctuation given in expression (2).[6] 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.

$$I_E = CI_0 \frac{\pi^2}{9R^2\lambda^4} \frac{(n^2-1)^2(n^2+2)^2}{n^4} KT\beta = I_0 \frac{\pi^2}{9R^2\lambda^4} KT\beta f_2(n) \qquad (2)$$

Where, I_O indicates irradiated-light intensity, R indicates the distance from a measurement target, λ indicates the wavelength of irradiated light, n indicates the complex refractive index of a media (liquid), K indicates a Boltzman's constant, T indicates absolute temperature, and β indicates isothermal compressibility. In this case, it is shown as a characteristic event that scattered-light intensity is proportional to the isothermal compressibility of liquid. The relation between the scattered-light intensity of liquid and the scattered-light intensity given from expression (2) is obtained. Liquid with different isothermal compressibility (β) is introduced into the particle detection volume (approximately 0.7 nL) of a particle counter that can detect a particle of 50 nm in size through the conversion of PSL particles in UPW so as to measure the intensity of the liquid's scattered light entering a photoelectric transducer. Figure 3 shows the relative relation between the scattered-light intensity and fluctuated- / scattered-light intensity of each liquid with the measured value of the scattered-light intensity in UPW and the calculated value of the fluctuated-light scattering as a standard. The value in a reference is used as the isothermal compressibility of each liquid.[6] There is good relation between the scattered-light intensity in liquid received using a particle counter and the scattered-light intensity in liquid which calculated based on the conception of fluctuated-light scattering.

A particle signal that is pulse-shaped and scattered light in liquid, which is DC light, can be separated by using the frequency band component of a signal. Therefore, the size of DC light is not directly related to the detection level of particles. For the photo-detector such as a photodiode, however, the level of the fluctuation (random) noise superimposed on an output signal generally increases depending on the quantity of incident light. Consequently, reducing the received quantity of the scattered light by a medium is effective to improve the detection performance of particle size in each liquid. In the signal processing band of the actual particle detection equipment described later, the level of fluctuation noise that the photo-detector of a photodiode outputs is about 2 to 3% of the scattered-light intensity, from liquid, to be received.

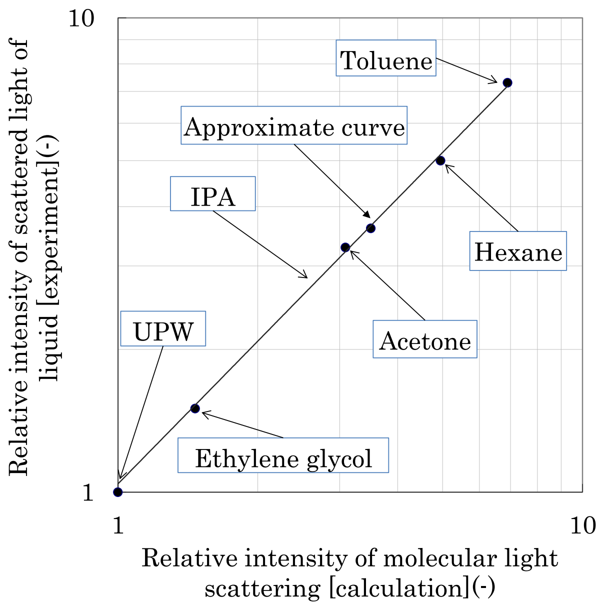


Fig.3 Light scattering intensity of liquid material.

4. Particle measurement in a polymer solution

Many polymer solutions of a photoresist are about several 10s or more in light-scattering intensities, as high as the liquid shown in Figure 3. Therefore, they exert a significant influence on the sensing signal of submicron particles. Contamination particles are often controlled by a particle counter for which a dedicated system has been in use for a long time. For the scattered light of a polymer solution to a wavelength that does not induce the photosensitive reaction of a polymer, a phenomenon occurring as the fluctuation scattering of liquid molecules shown in expression (2) as well as the characteristics (molecular weight, dielectric constant, and density) of the polymer is taken into consideration. The isothermal compressibility value of a polymer solution cannot be actually known with ease and significantly depends on the maldistribution (non-uniformity) or coagulation state (dissolution level) of a polymer. It is thus difficult to estimate the quantitative value of light-scattering intensity. Consequently, the critical evaluation of measurable particle size is experimentally required for a specific sample. In this case, the measurable particle size is critically evaluated with an ArF (immersion) photoresist, of about 10% in polymer concentration, which is often used in a state-of-the-art semiconductor process at present as a main target.

The threshold value for particle size discrimination in a liquid-borne particle counter sets depending on the conventional system in which the PSL particle detection sensitivity in UPW is used as a standard. Therefore, the detection of 100 nm particles in a polymer solution means that the detection sensitivity of 100-nm PSL particles inUPW exceeds the light noise caused by the light scattering in the polymer solution. In an ArF photoresist solution, it is confirmed that the level of the scattered-light intensity by 100 nm PSL particles in UPW is almost the same as that of the fluctuation noise caused by the scattered light in an appropriate photoresist solution of about 30 pL in the particle detection system of the conventional liquid-borne particle counter for 50 nm particles.

5. Configuration of a particle detection system

Figure 4 shows the outline of a particle detection system in a polymer solution. The entire flow path of a particle detection block is constituted by optically transparent quartz materials. The size of particles to be measured is much smaller than the irradiated wavelength. Therefore, Rayleigh's scattering theory in expression (1) can be applied for the scattering behavior of particles. The scattered-light intensity does not depend on the direction in which particles are scattered. The particles are scattered in all directions at equal intensity. This is prescribed as 90-degree sideway light scattering in which a wide collecting angle can be obtained and in which it is easy to suppress optical aberration. The second harmonic (wavelength: 532 nm, output: 500 mW) of a laser diode-pumped YVO_4 solid laser is used as the irradiated light. The receiving optics can be set in a position opposing the flow-line direction of a sample flow by using an L-shaped quartz flow cell for the 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 the irradiated light pass. Therefore, the passing position of the particles is determined using a multi-channel type photodiode. 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 the particle detection area or the detection sensitivity can be kept constant.

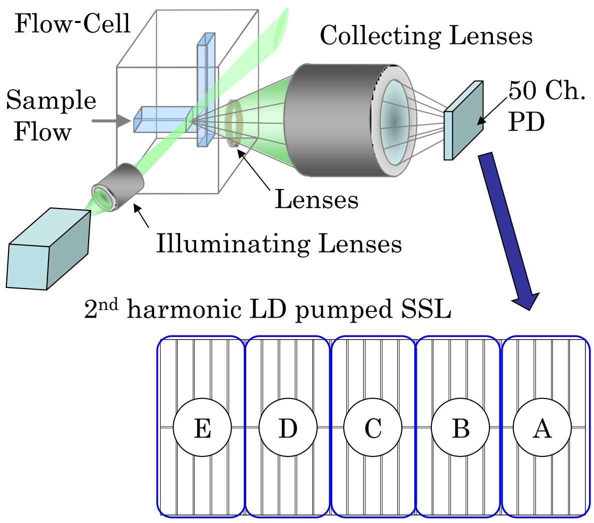


Fig.4 Block diagram of the new particle detection system.

With the improvement in the cleaning technology of photoresist products, it is necessary to measure the sample volume in which the number of particles not exceeding 1 particle/mL can be quantitatively evaluated in measurable particle size. On the other hand, the scattered light on the surface of quartz constituting a flow path is large as compared with the scattered light of particles. It is thus difficult to detect particles passing near the surface of the inner wall of the flow path. Therefore, the size of an effective particle detection area is prescribed by the visibility angle (field angle) of the receiving optics and the distribution of flow velocity in a path flow. To secure the counting difference between equipment for measuring equipment and the reproducibility of the measured value, with the detection efficiency of 50% as a standard, the effective sample flow rate is prescribed as 2.5 mL/min (sample flow rate: 5 mL/min) and the flow path's cross-section of a particle detection is prescribed as 0.48 mm^2, in consideration of the equipment configuration and the viscosity of the expected sample. The state in which 50% of the introduced particles pass is formed in a center area, which is about 20% of the flow path's cross-section, from the flow-velocity distribution of a sample flow by simulation. It is also confirmed that the measured value of counting efficiency with the concentration of the PSL particle test liquid as a standard is almost 50%.[7)]

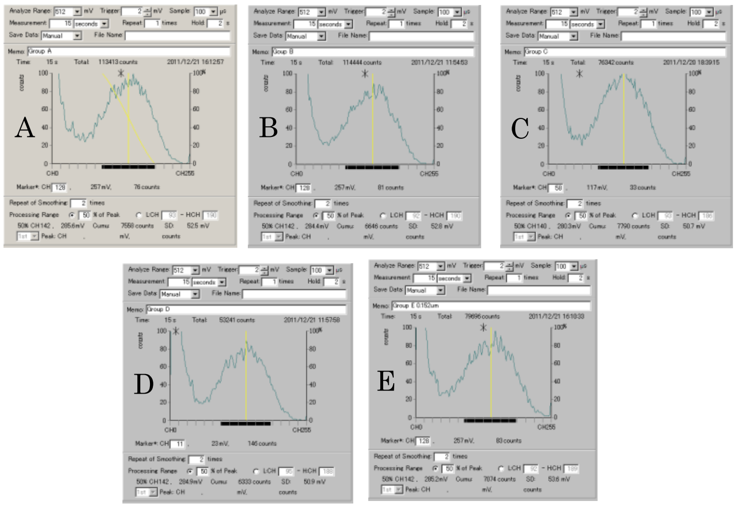
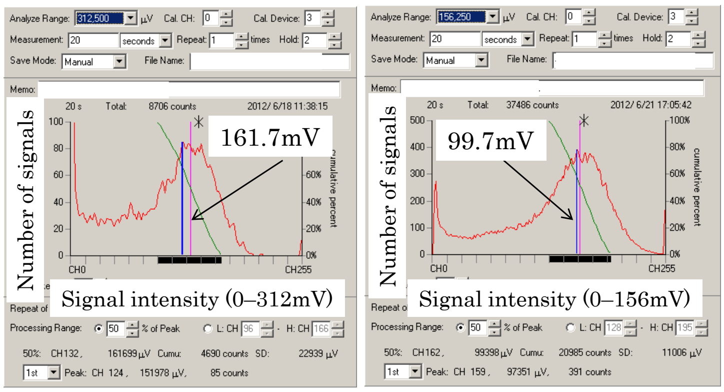


Fig.5 Performance of size resolution by multi-channel photodiode.

Laser rays through which particles pass are prescribed as approximately 10 μm in thickness, and the passing time of particles is prescribed as approximately 40 μsec, due to the actual restriction in equipment configuration (optical conditions, mechanical structure conditions, and signal processing conditions). The measured volume to be observed is approximately 1 nL because the cross-section of the particle detection area is prescribed in the form of a flow path. The particle detection area must be split into at the least 30 or more to ensure that particles with a size of 100 nm in an ArF photoresist solution can be detected. Actually, it was split into 50 channels (CH). As shown in Figure 4, 50 channels are collected as five groups 10 channels at a time. The crest value's distribution form of a 100 nm PSL particle-sensing signal in each group is shown in Figure 5. The horizontal axis in each figure indicates the level of a crest value, and the vertical axis indicates the frequency of signal



100nm PSL particles in UPW (ref. index:1.33)

100nm PSL particles in glycerin solution (ref. index: 1.4)

Fig.6 Dependence characteristic to the medium refractive index of particle detection performance.

generation. The form of distribution (particle size resolution: 3.4 to 3.7%) is almost the same. Detection characteristics do not depend on the position of the particle detection area. Quantitative characteristics are judged to have been secured in this case.

For a particle counter, the detection performance is adjusted and calibrated by the PSL particles in UPW. A concave lens surface is set in a flow path so as to suppress the change in focusing characteristics depending on the refractive index of the liquid. Figure 6 shows the detection characteristics of 100 nm PSL particles dispersed in a UPW and glycerin solution adjusted to refractive index 1.4. The particle size resolution is almost the same (2.3 to 2.7%). It is known that the form of signal distribution does not vary depending on the difference of a medium. The scattered-light intensity ratio of particles given from Mie's theory is approximately 1.63. It can also be confirmed that the ratio of the scattered-light intensity to the measured value 1.62 (= 161.7/99.7) is in good agreement. This shows that the characteristics of an optical system do not vary depending on the refractive index of a medium.

6. Performance of particles for a photoresist

The measurement example of a particle detection level in an ArF photoresist is shown in Figure 7. In this particle detection system, it was confirmed that a particle of 70 nm in size can be detected in the sample of UPW in which the light scattering by liquid can be ignored. About 50 sample noise levels of a product level with a different base solvent configuration or polymer concentration and a different polymer structure were measured . In all samples, the noise levels do not exceed the threshold value of particles with a size of 100 nm. It was confirmed that 100 nm particles in an ArF photoresist solvent can be measured by using a multi-channel photoelectric transducer. The S/N ratio of a particle of 100 nm in size widely varies in the range of about six times the normal one. This paper does not describe detailed information. However, this dispersion is not necessarily proportional to the polymer concentration or molecular weight. It is guessed that the dissolution state of a polymer is also related to the level of scattered light in liquid. In a detection sensitivity area of about 70 nm in particle size, the fluctuated/scattered light by a base solvent is completely suppressed by a multi-channel system. It is considered to exert no influence on this noise level.

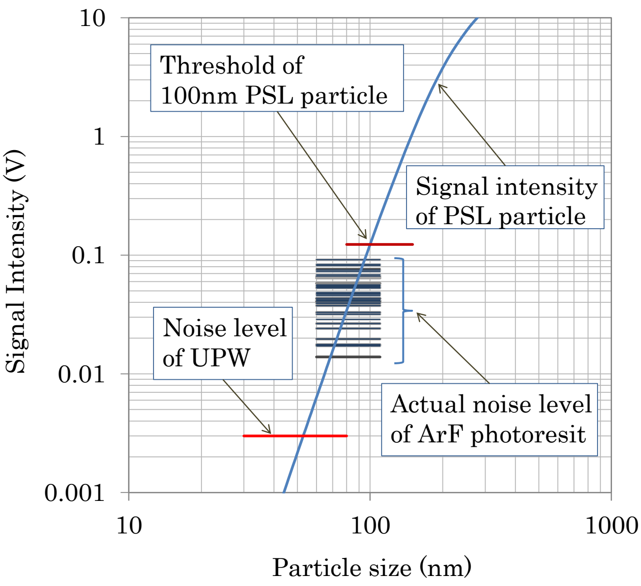


Fig.7 Detection performance of particles for ArF photoresist solution.

7. Reliability for the counted value of low-concentration particles

A particle counter is a measurement method suitable for the measurement of low-concentration particles. However, the minimum measurable concentration is limited by the false counting due to the random noise that a photodetector mainly generates and the light noise superimposed on laser rays. On the other hand, there are no practical methods other than a particle counter for ensuring that particles do not exist in the test sample. Therefore, it is not easy to evaluate the occurrence frequency of particle counter's false counting quantitatively by actual measurement. The random noise generated by a photodetector is mainly a self-generated noise occurring from an external high-energy elementary particle such as a cosmic ray or occurring from an element due to the electronic density fluctuation of the element itself. Therefore, the generation of a noise signal related to the photodetector is considered a random and discrete phenomenon in units of time. For the main light noise superimposed on laser rays, the intensity of laser rays temporarily fluctuates due to the longitudinal mode of the laser or the change in an extinction ratio. Consequently, such a noise signal is considered to be unevenly distributed in units of time and continuously counted at certain time intervals. The level of false counting contained in the measured value is estimated by obtaining the distribution of the occurrence frequency. Figure 8 shows the example given when particles with a size of 50 nm or more in UPW are measured continuously.[8)] The particles are 10-minute measured for about 80 hours to obtain the occurrence frequency of the counted value. The sample flow rate is 20 mL/min, and the counting efficiency of a particle counter is 10% (effective sample flow rate: 2 mL/min). The horizontal axis indicates the counted value per 10 minutes, and the vertical axis indicates the occurrence frequency of the counted value. This shows Poisson's distribution-shaped frequency distribution in which the average value (approximately 189/L) of all measured values generally overlaps with the maximum occurrence frequency.

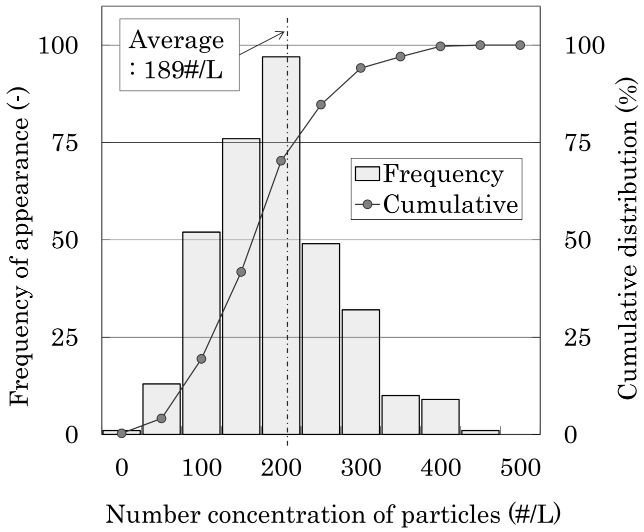


Fig.8 Frequency distribution of the counting of particles in UPW.

There is no phenomenon in which many particles are counted in a short time. The false counting due to laser rays is judged to be not contained. To estimate the occurrence frequency of false counting due to a photodetector, under the conditions in which light does not enter the receiving optics, the result obtained when the occurrence frequency of the false counting is measured at the threshold of the minimum measurable particle size is shown in Figure 9. Ten-minute measurement is continued 88 times. The average occurrence frequency of false counting is about 0.3 counts / 10 minutes. This is equivalent to 15 counts / L when converted using an effective sample (2 mL/min). 2σ on one side is equivalent to about 50 counts / L (one count / 10 minutes). Therefore, this

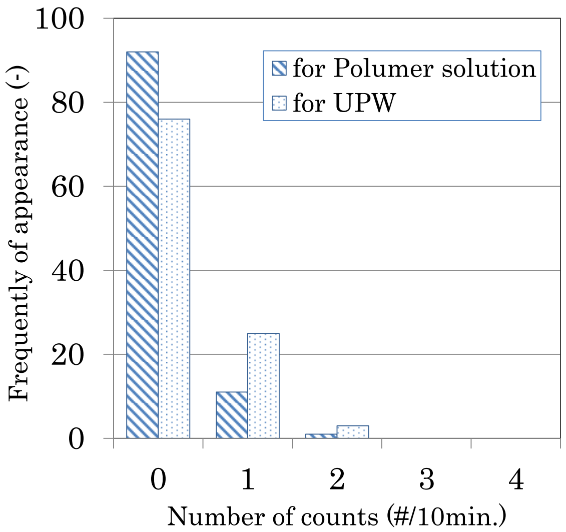


Fig.9 Occurrence probability of false counts.

shows that the measured value is barely influenced by false counting and that a particle count of about 50 count / L in UPW can be evaluated. In a particle counter for polymer solution, the average occurrence frequency of false counting equivalent to a particle of 70 nm in size is about 0.12 counts / 10 minutes. This is equivalent to 5 counts / L when converted using the effective sample (2.5 mL/min) of the particle counter. 2σ on one side is considered to be able to be evaluated as about 30 counts / L (0.7 counts / 10 minutes) according to the occurrence frequency of false counting due to a photoelectric transducer. It is necessary to confirm the false counting separately because the occurrence frequency of false counting is due to the equipment components of a particle counter and the particle size to be measured.

8. Conclusion

It could be confirmed by new particle detection technology that particles with a size of 100 nm or less in an ArF photoresist solvent can be detected in a practical level. In a particle counter for which a light-scattering phenomenon is used, light is also necessary to be irradiated on the medium in a particle detection area. In a particle counter that is used for particles of approximately 50 nm or less in size, many chemical materials that could be regarded to be optically transparent until now proved to indicate the light-scattering behavior that exerts a significant influence on the detection of particles. The necessity for the particle contamination control of materials (for example, the polymer solution of a photoresist or antireflection coating, or the new materials of a metallic complex or monomer-mixed liquid) that have a remarkable correlation with light is on the increase. The technology described in this paper is effective to suppress the scattered light in liquid molecules. This technology can also be expected to give a certain effect to the improvement in particle detection sensitivity in chemical materials when it is used in combination with technology for improving the particle detection sensitivity to be treated for UPW.

The particle concentration of the controlled particle size has been remarkably decreasing with the progress of the particle contamination control technology of liquid materials. Simultaneously with the detection of fine particle size, sharing the technology for keeping the quantitative characteristics of a particle concentration-measured value and its objective evaluation method is also considered to be important for the future particle control.

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