Real-Time Measurement of Exact Size and Refractive Index of Particles in Liquid by Flow Particle Tracking Method

T. Tabuchi, K. Bando, S. Kondo, H. Tomita, E. Shiobara, H. Hayashi, H. Kato, A. Nakamura, Y. Matsuura, and K. Kondo

***Abstract*—It is known that particle size obtained from Brownian motion of a particle is called the diffusion coefficient equivalent size (DCES) and is close to the geometric size independent of the physical properties of a particle. In this paper, it is described that real time measurement of the particle size and particle number concentration by observing the Brownian motion of the particles from which the influence of the flow field has been eliminated by the instrument combining the flow particle tracking (FPT) method and the L-shaped flow cell. Furthermore, we realized in evaluating the refractive index, which is the physical property information of the particles, from the DCES, the Rayleigh scattering equation and the light scattering intensity of particle that physical properties are known. In this paper, we also discuss that improvement of particle size accuracy and refractive index accuracy in the measurement of DCES.**

***Index Terms*—Brownian motion, diffusion coefficient equivalent size (DCES), flow particle tracking (FPT) method, physical properties of a particle, refractive index.**

I. Introduction

In WET process of semiconductor manufacturing such as lithography or cleaning, in order to reduce defects caused by particle contamination, it not only improves detection particle size, but it is becoming important to identify particle material.

Recent semiconductor roadmaps are requiring the management of difference of physical properties, such as "EAP (Electrical Active Particles)" and "non-EAP" [2].

Therefore, in addition to the performance of LSLPC (Light Scattering Liquid-borne Particle Counter) which measures particle size and particle number concentration, there is an increasing demand for instruments that can evaluate physical properties [3], [4]. So, we developed FPT instrument [1] that made it possible to measure the refractive index

Generally, the number concentration of particles in liquid has been classified with the light scattering equivalent size (LSES) by LSLPC. However, when the refractive index of the measured particles differed from the calibrated particles significantly, there has been a matter in which LSES differs from the geometric size. Meanwhile, DCES is obtained from the displacement of a particle by Brownian motion which does not depend on the physical properties of the particle, therefore DCES becomes close to the geometric size.

Furthermore, refractive index of the particle can be obtained by measuring the light scattering intensity of particles simultaneously with DCES measurement. By estimating the physical properties of the particle from the refractive index, it is expected to become information to pursue the cause of the generation of contamination particles.

If composition of contamination particles such as metal, fluororesin and bubbles can be estimated, it will be possible to take an action promptly and appropriately. Furthermore not only a yield improvement but an improvement in semiconductor development speed and the contribution to equipment starting are expected from it.

In addition, this FPT instrument enables real time measurement. Real time measurement makes it possible to perform analysis while the processing semiconductor manufacturing, which may significantly reduce the time to finding defects. In addition, by performing measurement *on-site*, contamination due to analysis can be reduced and more accurate judgment can be performed [5]. The method to realize real-time measurement is described in the "FPT INSTRUMENT" section of this paper.

II. FPT Instrument

Fig. 1 shows a schematic diagram of the FPT instrument. The Laser light (λ: 532 nm) shaped by the lenses (A) is irradiated on the sample flowing in the flow-cell, and the displacement of particles is measured with CMOS image sensor via a light receiving lenses (B).

The sample flow rate is 0.1 mL/min, and the interval for tracking the displacement of particles with CMOS image sensor is 120 fps. Fig. 2 is a basic concept of new FPT

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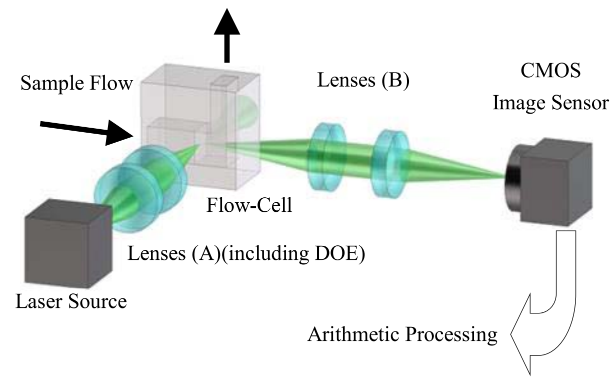

Fig. 1. Schematic diagram of the FPT instrument.

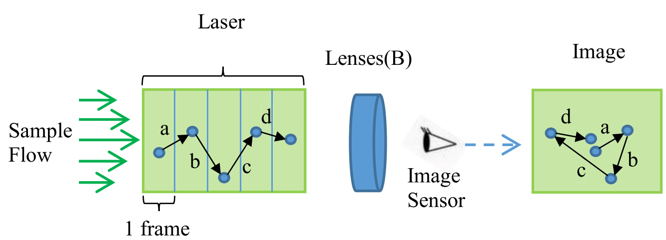

Fig. 2. Image of particle tracking.

method which shows the tracking displacement of particles. The displacement of particle was tracked during per frame as the particles in the flow field pass through the illumination light. At the image sensor, the particles are observed as shown in the right side image (a to d). Particles are tracked several times, while passing in the irradiation light. Reliability of DCES obtained by Brownian motion is improved by averaging multiple displacements.

In Section IV (Experiment & RESULT), the averaged numbers of displacements were about 10. By analyzing the captured images in real time, DCES and the refractive index can be obtained continuously.

In addition, the laser light to irradiate is making energy intensity distribution uniform using the diffractive optical element (DOE). As a result, the energy intensity in the observation plane becomes uniform (from Gaussian to Top Hat Shape), which contributes to the improvement of particle size and refractive index.

Fig. 3 shows the simulation of fluid velocity distribution around the particle detection area in the flow cell. The path is L-shaped, and the sample fluid flows from left to right and further upward. An observation surface is set in the horizontal plane of the flow path, and the displacement of particles is measured by the image sensor via light receiving lenses (B) [6], [7].

As can be seen from Fig. 3, it is understood that the laminar flow state is good in the observation plane. By adopting the L-shaped flow cell, it becomes possible to observe the particles from the direction opposite to the flow direction of the sample, and it is possible to eliminate the influence of the particle behavior by flowline. The result of the simulation is confirmed that the deviation of streamline vectors other than Y direction is less than 10 % of the expected displacement by Brownian motion of 100 nm particles in UPW.

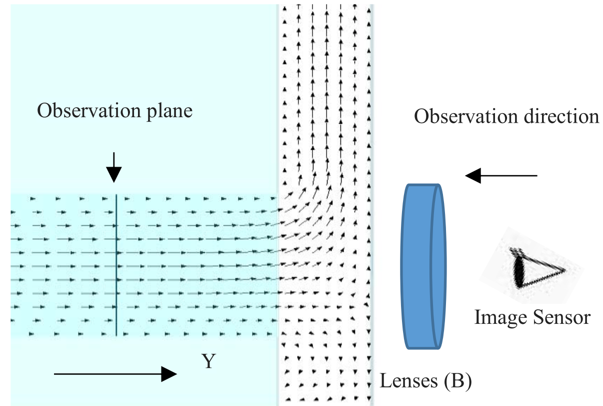

Fig. 3. Simulation of fluid velocity distribution in L-shaped flow cell.

III. DCES and Refractive Index Calculation Method

DCES(D_p) is obtained from Stokes-Einstein's law shown in equation (1) [8].

$$D_p = \frac{K_B T}{3\pi \eta D} \tag{1}$$

And, the diffusion coefficient of a particle D is expressed by equation (2).

$$D = \frac{< L^2 >}{t} \tag{2}$$

where, K_B : Boltzmann constant, T : temperature of fluid, η : fluid viscosity, L : displacement of a particle per time t, $<>$: mean-square displacement.

As shown in equations (1) and (2), since the displacement of particles due to Brownian motion is inversely proportional to the $1/2$ power of a particle size, the smaller the particle, the greater the displacement.

It can be seen that the size of particles is not dependent on the physical properties of particles and it is only depending on the temperature and viscosity of fluid.

The particles perform Brownian motion in a three-dimensional direction, but since the image sensor observes only movement in a two-dimensional direction, equation (1) is using the two-dimensional model of diffusion coefficient.

Meanwhile, at tIt can be seen that the size of particles is not dependent on the physicahe same time with measuring the DCES, the light scattering intensity of each particle is measured, and the relation of the scattering intensity and estimated refractive index of a paticle is shown by obtained from the Rayleigh scattering given by equation (3) [9].

$$I(\theta) = I_0 \frac{\pi^4 d^6}{8R^2\lambda^4} \left(\frac{\left(\frac{n_p}{n_s}\right)^2 - 1}{\left(\frac{n_p}{n_s}\right)^2 + 2} \right)^2 \left(1 + cos^2\theta\right) \tag{3}$$

where, $I(\theta)$: light scattering intensity of a particle in the direction of the crossing angle θ with the irradiation light direction, R : distance between particle and light scattering intensity observation position, I_0 : irradiation light intensity, λ : irradiation light wavelength, d_a : particle size of calibration particle, d_b : measured diffusion coefficient equivalent

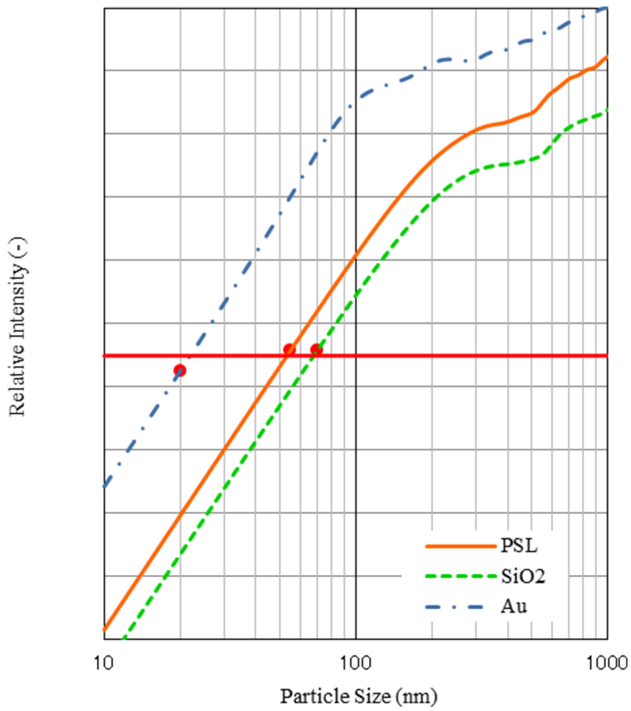

Fig. 4. Relative light scattering intensity in UPW (The Mie scattering equation).

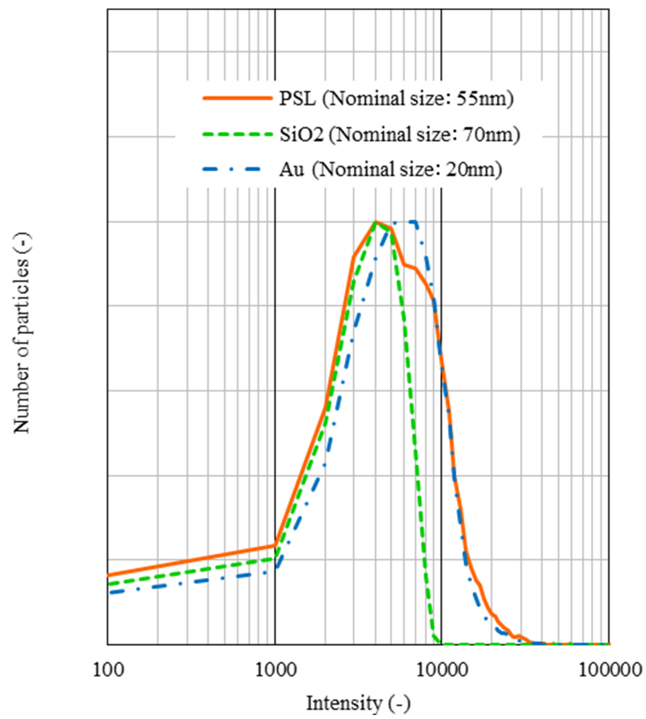

Fig. 5. Distribution of light scattering intensity of particles in UPW.

size, n_{pa} : refractive index of the calibrated particle, n_{pb} : refractive index of the measured particle, n_{pb} : refractive index of sample fluid for calibration, n_{sb} : refractive index of measured sample fluid.

Beforehand, the relation of physical properties and light scattering intensity of known particles are measured. From equation (3), light scattering intensity of the calibrated particle is made a correlation with the nominal particle size and the refractive index, so the relation constant can be decided. As a result, the refractive index of the particle shown in equation (4) is obtained from constant and DCES, light scattering intensity of the particle.

$$n_{pb} = n_{sb}\sqrt{\frac{3}{1 \pm \sqrt{\frac{I_b}{I_a}\left(\frac{\frac{n_{pa}^2}{n_{sa}}-1}{\frac{n_{pa}^2}{n_{sa}}+2}\right)^2\left(\frac{d_a}{d_b}\right)^6}} - 2} \tag{4}$$

As can be seen from equation (4), two solutions are calculated. If the relative ratio between the refractive index of medium and particles is almost same, it means that a light scattering phenomenon at nearly same intensity occurs.

In addition, DCES and the refractive index are continuously obtained in real time by converting the position coordinates and light scattering intensity of the captured particles into numerical values for each frame simultaneously, and executing correlation between frames by numerical processing.

IV. Experiment & Result

PSL particles (nominal size: 55 nm), SiO_2 particles (70 nm) and Au colloid particles (20 nm), which are observed to be approximately equivalent in LSES, were measured particle sizes and compared with the nominal sizes [10].

Fig. 4 shows the relationship between relative light scattering intensities of particles and particle size of physical properties, respectively.

The horizontal axis represents particle size, and the vertical axis represents relative light scattering intensity. The relative light scattering intensity was calculated from the Mie scattering equation. Three points in the Fig. 4 represent relative intensities of PSL particles (nominal size: 55 nm), SiO_2 particles (70 nm) and Au colloid particles (20 nm). It can be seen from the horizontal line in Fig. 4 that the light scattering intensities of the particles having the respective sizes and physical properties are almost the same. Although the light scattering intensity of particles can be determined by Mie scattering equation, it is known that the Rayleigh scattering equation approximates in the small particle size region, so the refractive index calculation described in this paper uses the Rayleigh scattering equation.

Fig. 5 shows the number frequency distribution of measured light scattering intensity of each particle. The horizontal axis represents relative light scattering intensities of each particle, and the vertical axis represents relative frequency. Each Number of particles is normalized. Fig. 5 shows that the light scattering intensities of these particles are almost the same. Therefore, it is difficult to distinguish them as LSES.

Meanwhile, these particles were measured by the FPT method and the particle sizes were determined respectively, and the result is shown in Fig. 6. The horizontal axis represents the measured particle size and the vertical axis represents the relative number frequency. Each number of

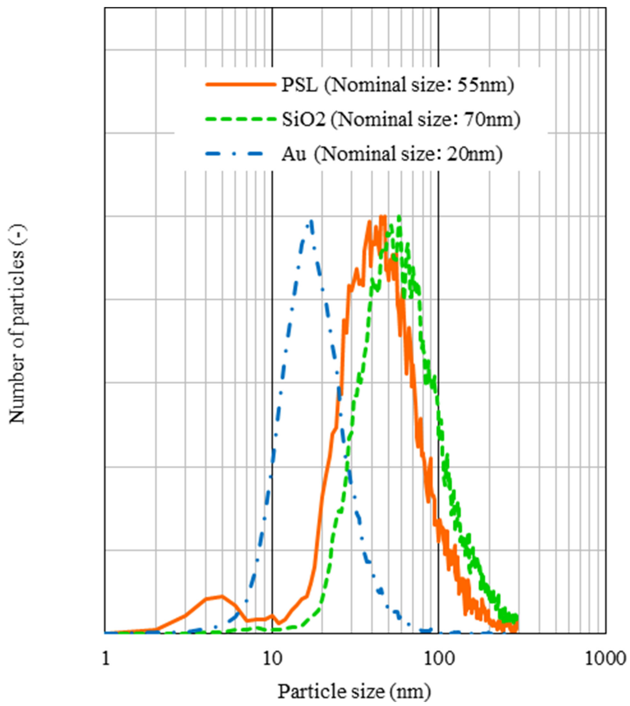

Fig. 6. DCES distribution of particles in UPW.

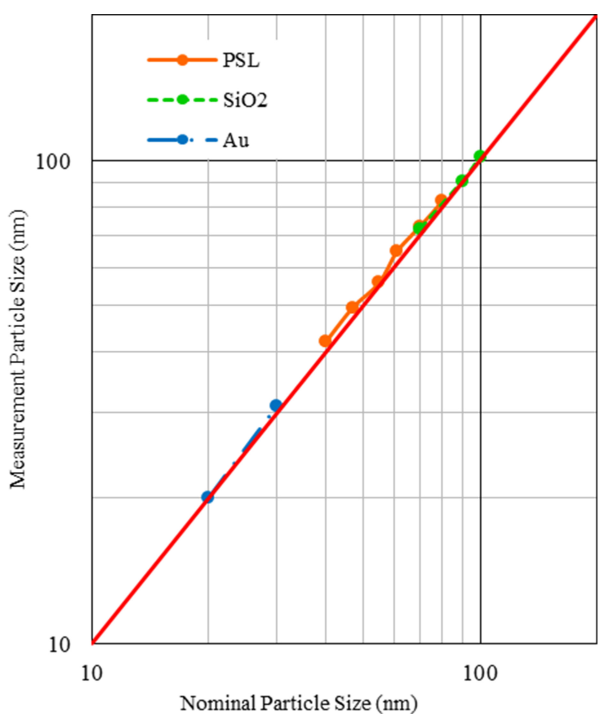

Fig. 7. Relation of DCES and nominal size of particles in UPW.

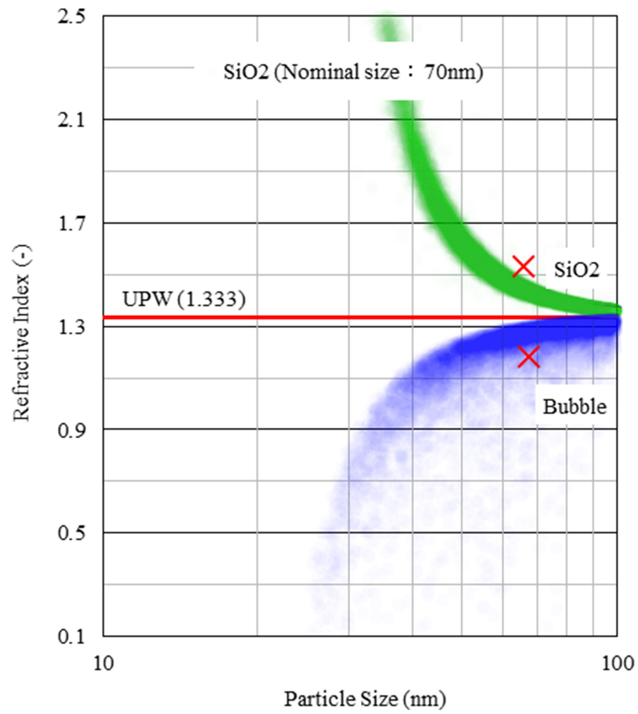

Fig. 8. Number frequency distribution mapped with DCES and a refractive index of particles in UPW.

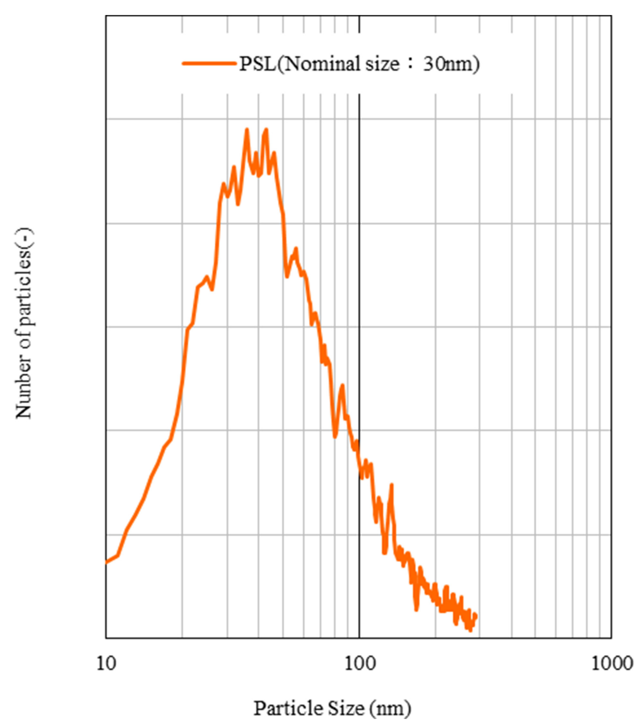

Fig. 9. DCES distribution of particles in UPW.

particles is normalized. As can be seen from Fig. 6, it is suggested that FPT method is able to distinguish the geometric particle size.

Fig. 7 shows the results of measurement of monodisperse particles of several kinds of physical properties and particle sizes. The horizontal axis represents the nominal particle size, and the vertical axis represents the particle size measured by the FPT method. The red line in the Fig. 7 represents the ideal line where the nominal particle size and the measurement particle size are equal.

As can be seen from Fig. 7, even if the components of particles are different, it turned out that DCES and nominal particle size are well in agreement.

Next, bubbles generated by the gas dissolving equipment were mixed with 70 nm SiO_2 particles, and measured

DCES and the refractive index respectively. Fig. 8 shows the 2-dimensional histogram of particle numbers composited by the DCES and the refractive index of particles. The horizontal axis represents the particle size, and the vertical axis represents the refractive index. As can be seen from Fig. 8, it was confirmed that the medians of the measured refractive index almost well agree with the known refractive index [11].

The accuracy of measured refractive index depends on the observation accuracy of the particle size and light scattering intensity. Even if the light scattering intensity of a particle is measured correctly, in case where the particle size is obtained smaller than the actual particle size due to the observation error of the Brownian motion, the refractive index is measured larger than the known value. As a result, even if monodispersed particles are measured, the measurement sizes are distributed widely.

By Improvement of the measurement accuracy of DCES, it can be estimated that the measured value of a refractive index also improves.

Finally, the minimum particle sensitivity of this FPT instrument was estimated as shown in Fig. 9. The horizontal axis represents the measured particle size and the vertical axis represents the relative number frequency. PSL particles of 30 nm nominal size in UPW were measured and a monodisperse distribution and adequate measurement particle size were able to be obtained. Therefore, it was found that this FPT instrument can measure as particles the light intensity in which at least 30nm particles in UPW are scattered.

In FPT instrument, the definition of the measurable particle size needs to be discussed since the range of measurable particle size varies with the relative refractive index.

V. Conclusion

We succeeded in development of new instrument, which uses FPT method, that measures the displacement of particles by Brownian motion except the influence of flow field, and it is able to measure DCES (close to the geometric size) and the number concentration of particles in real time. Furthermore, it made it possible to identify refractive index of particles by simultaneously measuring DCES and light scattering intensity of particles.

We would like to expect that estimating the particle material from the refractive index of the particles by the FPT method will be contributed to improve actual contamination control.

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