DEVELOPMENT OF THE PRIMARY NANOPARTICLE MEASUREMENT STANDARD BY THE ELECTRO-GRAVITATIONAL AEROSOL BALANCE

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INTRODUCTION
Nanoparticle characterization has been critical in semiconductor industry, as the feature size of IC continuously shrinks to increase the density of chips in one circuit. The standardization and metrology of nanoparticle characterization are important areas of metrology, though they can be difficult because nanoscale resolution is frequently required. In order to characterize the nanoparticles in nanoscale accuracy, metrology tools are required to detect and analyze these nanoparticles for identifying the sources of the contamination. However, due to lack of calibration standards, inconsistent measurement results are observed for nanoparticle characterizations while different measurement techniques were used [1]. Therefore, in order to accurately and consistently determine the sizes of the nanoparticles, establishments of measurement standards in nanometer range become crucial and necessary.

A primary standard, based on the electro-gravitational aerosol balance (EAB) [2, 3], has been developed at Center for Measurement Standards for nanoparticle sizes ranging from 100 nm to 500 nm in diameter. In this method, charged particles are introduced into the space between horizontally placed planar electrodes. Survival function, defined as the ratio of the number of particles left after holding time to the initial number of particles as a function of the particle mass, is used to evaluate the balance between the electrostatic and gravitational forces exerted on the particles. Based on the evaluation, with known particle mass and particle density, the particle diameter is derived. Since the measurement principle is the simple, this method is expected to achieve high accuracy and low uncertainty. The calibrated or certified particles by this primary standard system with superior uncertainty are used for the calibration of other particle measuring equipment in industry.

THEORY
Two electrodes (stainless steel plates) are placed parallel in a distance $H$ to form a gap to generate an electric field with a voltage $V$. At initial stage, assuming $t = 0$, monodispersed particles with electric charge uniformly distribute inside of the two electrodes. As shown in Figure 1, balance can be obtained between the static electric force $F_E$, assumed in the upward direction, and the gravity force $F_G$ (downward) on a charged particle. After a relaxation time, $\tau$, the particle will move at a constant terminal velocity, $\nu$. The terminal velocity, assumed to be in the upward direction, can be represented as:

$$\nu = \tau \left[ \frac{q e V}{m H} - (1 - \frac{\rho_a}{\rho_p}) g \right]$$

(1)

where $e$ is single electric charge, $q$ is the number of static charge on a particle, $m$ is the mass of a single particle, and $g$ is the standard gravitation. In addition, $\rho_a$ and $\rho_p$ are the densities of the air and a particle, respectively.

Furthermore, the relaxation time, $\tau$, is related to the size of the particle, $d_p$, the density of the particle, $\rho_p$, and the gas viscosity, $\eta$, as shown in below:

$$\tau = \frac{d_p^2 \rho_p}{18 \eta} C_w(d_p)$$

(2)
where $C_d(d_p)$ is the Cunningham slip correction factor that corrects the non-continuum gas behavior of the drag force for small particles. Due to the terminal velocity, the monodispersed particles move in the upward direction. A portion of the charged particles will stop on the top electrode plate after a holding time, $t_h$, and a clear space without particles will be formed near the bottom of the electrode plate, as shown in Figure 1. A residual particle ratio can be defined as the numbers of particles at $t = t_h$ to the numbers of particles at $t = 0$. The survival function, $s(m, V)$, is used to describe the ratio as:

$$s(m, V) = \begin{cases} 1 - v \cdot t_h / H, & \text{if } t_h \leq H / v \\ 0, & \text{Otherwise} \end{cases}$$ (3)

where the $s(m, V)$ is the survival function of the mass of the particle and the charge, $V$. A slightly distorted isosceles triangle survival function can be obtained according to the mass of the particle, as shown in Figure 2. Three mass numbers mirrored to the 3 poles of the triangle can be used to decide the size of particles: the first two, $m_\pm$, are the triangle poles on the base line, and the third one is the top pole of the triangle at point $m_0$, where the survival function $s(m, V)$ is equal to 1. The $m_0$ and $m_\pm$ can be determined by the following equations as:

$$m_0 = \frac{qeV}{(1 - \rho_a / \rho_p)Hg}$$ (4)

$$m_\pm = \frac{qeV}{[(1 - \rho_a / \rho_p)g \pm H / t_h \tau]H}$$ (5)

The $m_0$ represents the average mass of the particles. Accordingly, the average size of the particles, $d_{p0}$, can be calculated by a known average mass, $m_0$, as:

$$d_{p0} = \left(\frac{6m_0}{\pi \cdot \rho_p}\right)^{1/3}$$

FIGURE 2. Survival function is an isosceles triangle.

MEASUREMENT SYSTEM

The system setup and the measurement procedure in this study are similar to that of Ehara et al. [2, 3]. A schematic diagram for the system of the primary standard in this study is shown in Figure 3. The system consists of an aerosol generator, a charge neutralizer, a differential mobility analyzer, a pair of dc voltage sources, a digital multi-meter, a thermometer, a condensation particle counter and homemade electrodes.

FIGURE 3. Diagrammatic sketch of the electro-gravitational aerosol balance.
The two flat plate electrodes made of stainless steel, 280 mm in diameter and 10 mm in thickness are separated by an alumina annulus. The nominal dimensions of the alumina annulus are 15 mm in height, 210 mm in internal diameter, and 250 mm in external diameter. The volume of the sealed space is, then, 519.54 cm$^3$. Furthermore, there are twelve openings circumnavigated on the side of the alumina annulus: five of which serve as aerosol inlets, five as clean air inlets, and the remaining two as aerosol outlets. One of the functions for the aerosol outlets is to exhaust the aerosol before the holding time has started, and the other one provides the aerosol to the condensation particle counter after the holding time has elapsed. The flatness of the electrodes and the alumina annulus were evaluated with a computer-generated hologram interferometer, as shown in Figure 4. The PV values of the electrodes and the alumina annulus are less than 2 $\mu$m and 4 $\mu$m, respectively. The voltage of the electrodes is supplied by the pair of dc voltage sources (Model 2410, Keithley Instruments Inc.), and monitored by the digital multi-meter (Model 2010, Keithley Instruments Inc.).

The positively charged particles in the sealed space will be evaluated to determine the sizes of nanoparticles.

The liquid suspending particles is first conveyed into the gas phase using the aerosol generator (Aeromaster-V, JSR Corp.). The resulting droplets pass through the Am-241 charge neutralizer where the droplets and charged ions collide to generate charge distributed as a modified Boltzmann distribution. The differential mobility analyzer (Model 3080L, TSI Inc.) is installed on the top of the electrodes in order to filter out the multiply charged particles. As a result, all particles introduced into the space between the parallel plate electrodes are singly charged. After a certainty holding time, particles will be stabilized due to the balance of electrostatic force and the gravitational force. The condensation particle counter (Model 3775, TSI Inc.) counts the number of particles passing through the detector per cubic centimeter of gas flow. In addition, the electrodes are held in an adiabatic vessel to obtain a uniform temperature over the two electrode surfaces, in order to suppress thermophoresis of particles. Consequently, a certain fraction of the particles is deposited on the electrode surfaces from the space between the electrodes. The survival function is used to describe the ratio of the number of particles left after the holding time to the initial number of particles. The particle survival rate, defined as a function of the voltage applied to the electrodes, is used to determine the particle mass. Once the particle density is known, the particle size is calculated and determined.

RESULTS

The specification of the tested sample, JSR SC-048-S, is shown in Table 1. The experimental parameters for employing the differential mobility analyzer are shown in Table 2, and the holding time is set at 45 minutes. The seven measurement data of survival rates is shown in Table 3. The average diameter determined by the primary nanoparticle size standard system is 474 nm, and the best fit survival rate spectrum is shown in Figure 5. The certified diameter provided by the manufacturer is 479 nm, which agrees with the measurement results within 1% difference.

CONCLUSIONS

In order to achieve higher accuracy and lower uncertainty for nanoparticle size measurement, the electro-gravitational aerosol balance method has been used to develop the primary nanoparticle size standard system at Center for Measurement Standards, because of the
simplicity of its principle. The measurements for the particle sizes ranging from 100 nm to 500 nm are currently in progress.

It would definitely improve measurement consistency and accuracy if there exist particulate reference standards, international or industrial standards that would sufficiently comprehend details of the measurements. Additionally, measurement consistency and accuracy could be improved, if the nanoscale instruments in the laboratories can be properly evaluated with uncertainty budget, and validated with recognized protocols.

REFERENCES


TABLE 1. Attributes of the tested polystyrene latex particles, JSR SC-048-S.

<table>
<thead>
<tr>
<th>Mean Diameter (nm)</th>
<th>Uncertainty (k = 2)</th>
<th>Standard Deviation (nm)</th>
<th>CV</th>
<th>Specific Gravity</th>
<th>Number Concentration</th>
<th>Solid Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>479</td>
<td>15</td>
<td>4.79</td>
<td>1.0%</td>
<td>1.054</td>
<td>1.6 ( \times ) 10^{11} #/ml</td>
<td>1%</td>
</tr>
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</table>

TABLE 2. Experimental parameters of the differential mobility analyzer.

<table>
<thead>
<tr>
<th>Set Voltage</th>
<th>Sheath Air Flow Rate</th>
<th>Main Outlet Flow Rate</th>
<th>Aerosol Flow Rate</th>
<th>Sample Flow Rate</th>
<th>Relative resolution</th>
<th>Trapezoidal-city</th>
</tr>
</thead>
<tbody>
<tr>
<td>9905 V</td>
<td>5.40 lpm</td>
<td>6.17 lpm</td>
<td>1.54 lpm</td>
<td>0.77 lpm</td>
<td>0.20</td>
<td>0.33</td>
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</tbody>
</table>

TABLE 3. Measurement data produced by the primary nanoparticle size standard system.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Survival Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.052</td>
<td>0.00872</td>
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<tr>
<td>32.961</td>
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<td>42.998</td>
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