Recent Development of Differential Mobility Analyzers For Size-Classification of Nanoparticles and Their Applications to Nanotechnologies

Kwang Soo Seol *, Yoshimichi Ohki ** and Kazuo Takeuchi *

Abstract - The present paper gives a review of the recent development of a differential mobility analyzer (DMA) available for both particle size measurements and production of monodisperse particles in the nanometer range. Operating principles of a general DMA are introduced as well as characteristics of highly functional DMAs such as those capable of classifying particles in a measurement range as broad as 1-1000 nm at low pressures. Some examples of DMA applications are also described.

Keywords: Differential mobility analyzer, nanoparticles, nanotechnology

1. Introduction

The size of a particle is an important parameter for characterizing its behavior, and this is especially the case for nanoparticles. Nanoparticles formed in either a chemical or physical process are of interest in the field of materials science since they have properties significantly different from their bulk, while those attracting attention in semiconductor fabrication processes are contaminants that decrease the device performance. For these reasons, technologies to measure and classify the size of nanoparticles and to yield monodisperse nanoparticles have become important. For this purpose, a differential mobility analyzer (DMA) has been developed that classifies particles by passing charged ones through two concentric electrodes, between which an electric field is applied.

The history of a DMA dates back to the early 1900s [1]. After the first DMA was devised in 1920 by Erikson et al. [2], its performance and structure have been so significantly improved as to allow measurement and classification of charged particles of a submicrometer size with a high sensitivity at one atmosphere. The recent boom in nanotechnology has accelerated the improvement of a DMA to such an extent that it has enabled us to measure and classify particles with sizes ranging from one to several hundred nanometers even at low pressures [3-8]. In this review, we introduce various types of DMAs, focusing on their operating principles and applications to measurement of cluster sizes and synthesis of monodisperse nanoparticles.

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2. Operating Principles of Various DMAs

2.1 Basic principle

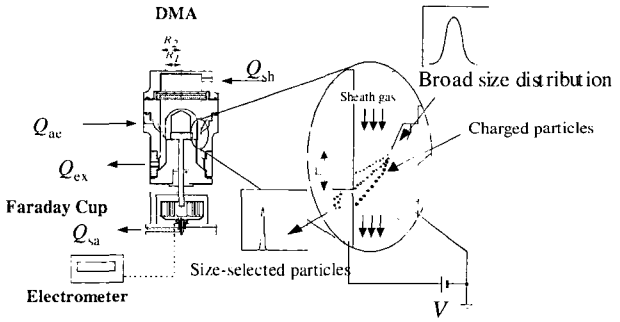

Fig. 1 Schematic of a DMA. Here, Q_{ae}, Q_{sh}, Q_{sa}, and Q_{ex} indicate an aerosol gas flow, a sheath gas flow, a sampling gas flow, and an excess gas flow, respectively.

A DMA essentially consists of a pair of either radial or cylindrical electrodes [9, 10]. Fig. 1 illustrates the basic operating principle of a cylindrical-type DMA. A sheath gas flows downward at a rate of Q_{sh} between the inner and outer cylindrical electrodes, into which an aerosol gas containing particles is supplied through an inlet slit at the top of the outer electrode at a flow rate of Q_{ae}. The particles dispersed in the aerosol gas flow were either positively or negatively charged by a particle charger placed before the DMA. A dc voltage ranging from 1 V to 10 kV is applied to the inner electrode in order to attract charged particles that drift down inside the DMA together with the sheath gas. Since smaller particles have a higher mobility and move faster across the interspace between the electrodes,

they reach the inner electrode at a relatively upstream position, whereas larger ones reach it downstream as shown in the ellipsoidal inset in Fig. 1. This means that the particles arrive at different points depending on their particle size D_p. Therefore, at a constant voltage, only the particles possessing a certain particle size can pass through an outlet slit on the inner electrode. The classified particles are then introduced to a Faraday cup electrometer for measuring their number concentration or the number of charged particles per unit gas volume. The total number concentration including neutral non-charged particles can be calculated using the known charging coefficient of particles [11]. Thus, the size distribution is obtainable by changing the applied voltage V.

2.2 DMA with a wide measurement range

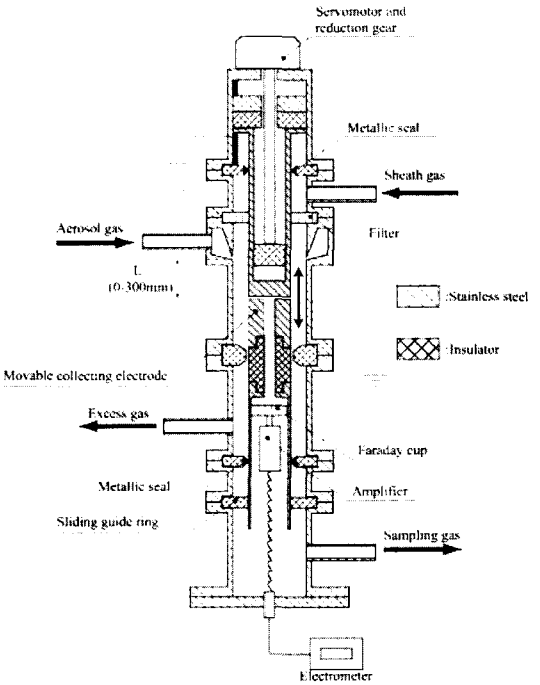

Fig. 2 Schematic of an adjustable-column length DMA (ACLDMA).

The measurement range of a DMA is limited by two physical phenomena: particle diffusion and electrical discharge between the DMA electrodes. When the applied voltage exceeds the breakdown voltage of the sheath gas, electrical discharge occurs, which sets the upper limit of the particle size measurable by a DMA. On the other hand, the resolution in the DMA size-classification of particles deteriorates due to particle diffusion that becomes significant as the particle size decreases. Consequently, the diffusion sets the lower limit of the measurable size. It is considered that the diffusion is effectively suppressed if the column length L between the aerosol inlet and outlet is short [12]. Therefore, DMAs with a short column (typically L= 16-18 mm) is used for the measurement of nanoparticles. For submicometer particles, DMAs with L > 100 mm are employed. Therefore, there is not a single regular DMA that can measure both nanometer- and submicrometer-sized particles.

Many aerosol reactors generate particles with sizes ranging from 1 to 10^3 nm. Therefore, a wide-range DMA is required. For a cylindrical DMA, D_p can be expressed by the following equation [9],

$$D_p = \frac{2n_p e C_c L V}{3\mu Q_{sh} \ln(R_2 / R_1)} \quad (1)$$

where n_p, e, C_c and μ are the number of charges, the elementary charge, the Cunningham correction factor, and the gas viscosity, respectively. Note that R_1 and R_2 are indicated in Fig. 1. According to Eq. (1), either an increase in L or a decrease in Q_{sh} increases the measurable maximum D_p, i. e., D_p at the breakdown voltage. The particle diffusion effects on DMA classification characteristics are approximately in inverse proportion to the migration Peclét number, which is simply expressed by the ratio of the characteristic time for migration through the path length in the particle migration direction to the characteristic time for the diffusion through the same distance [13]. Therefore, either a short migration distance or time for particle size classification, i.e., short L or large Q_{sh}, effectively reduces the particle diffusion effects regarding the DMA performance. Taking this principle into consideration, a method of controlling Q_{sh} as a function of D_p has been suggested for broad-range measurements of particle size [14]. In this method, Q_{sh} decreases as V increases. Therefore, for this flow-rate controlling method, the resolution of the DMA corresponding to a given Q_{ae}/Q_{sh} becomes low and the measurable particle size distribution becomes coarse as D_p increases.

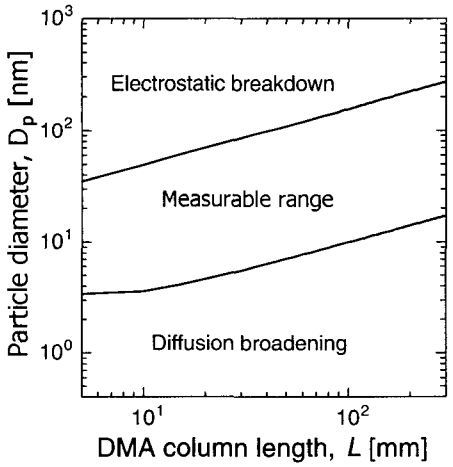

Fig. 3 Particle size measurement range of a DMA vs. DMA column length.

In order to compensate for this drawback, an adjustable-column length DMA (ACLDMA) has recently been developed where L is continuously variable between 0 and 300 mm [6]. Fig. 2 shows a schematic of the developed ACLDMA, which is characterized by a movable inner electrode. Fig. 3 shows the calculated range of DMA measurable size as a function of L, when the variables are assumed as Q_{ae} = 1 standard liter per minute (SLM), Q_{sh} = 10 SLM, R_1=25 mm, and R_2=33 mm[6]. In comparison with the flow-rate controlling method, the ACLDMA supplies the same resolution throughout the whole particle-size range.

2.3 DMA for low-pressure use

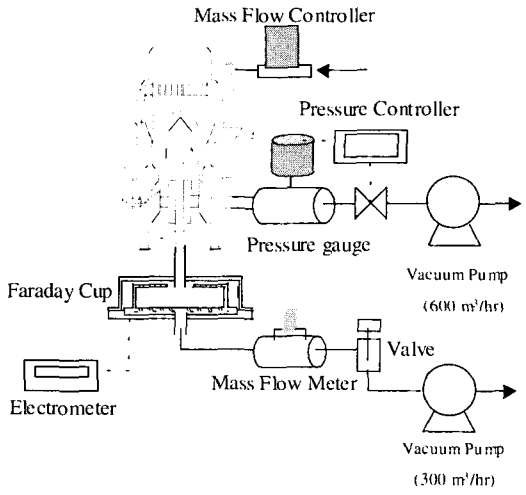

Fig. 4 Schematic of a low pressure DMA.

Fabrication processes using plasmas are currently indispensable for manufacture of semiconductor devices. However, since plasmas are chemically very active, they are prone to produce many particles which degrade the device properties. On the other hand, the line width of ultra-large-scale-integrated circuits (ULSI) has become even narrower, reaching approximately 100 nm in 1-Gbit ULSI. In this situation, the size of particles that may cause a problem is roughly estimated to be several ten nanometers. Therefore, a dependable monitoring method of nanoparticles is needed for the ULSI manufacturing processes, especially for those using low-pressure reactors such as plasma reactors. Two methods utilizing light scattering and electron microscopy have been used for the measurement of particles [15, 16]. However, the light scattering method is insensitive to particles smaller than the wavelength (approximately several hundred nm) of the probing light, whereas the electron microscopy method is not suitable for *in situ* monitoring.

A low pressure DMA (LPDMA) shown in Fig. 4 has been developed in order to realize *in situ* measurement of nanoparticles [5]. The DMA pressure of approximately 100 Pa has been achieved by increasing the gas flow conductance of a DMA and using vacuum pumps with high exhaust rates[5]. A Faraday cup electrometer with high flow conductance has been specially developed for measuring the number concentration of the charged nanoparticles at low pressures [5]. In general, the particle size classification of a DMA is characterized by a transfer function [9], which corresponds to the output of the size-classified particles as a function of particle mobility. On the condition that the particle diffusion is negligible, the transfer function $f(Z, Z^*)$ can be described as follows by an isosceles triangle function of the particle mobility Z with a centroid mobility Z^*:

$$f(Z,Z^*)=\frac{\alpha}{\beta}\left[\left|\frac{Z}{Z^*}-(1+\beta)\right|+\left|\frac{Z}{Z^*}-(1-\beta)\right|-2\left|\frac{Z}{Z^*}-1\right|\right] \quad (2)$$

where α and β are parameters determining the height and full width at half maximum (FWHM) of the transfer function, respectively. The area of the transfer function corresponds to classification efficiency whereas the inverse value of the FWHM corresponds to the resolution. As shown in Fig. 5, both α and β remain constant regardless of the DMA pressure being changed from one atmosphere (~100 kPa) to approximately 0.1 kPa [5]. This ascertains the normal operation of the DMA in the above pressure range. It is also notable that the minimum pressure for DMA operation is around 10^{-1} Pa. At this pressure, the mean free path of the gas molecules inside the DMA reaches several mm. In this situation, the sheath gas flow becomes a free molecular type and it cannot be separated from the aerosol gas flow. Therefore, neither the nanoparticle streamline shown in Fig. 1 is formed, nor the DMA operating principle is valid.

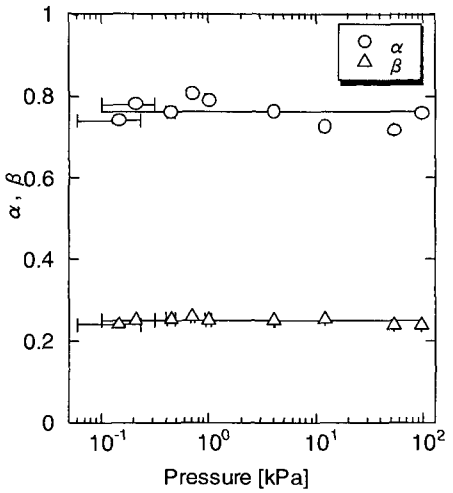

Fig. 5 Dependence of height α and half width β of a DMA transfer function on the operating pressure.

Figs 6 (a) and (b) show examples of size distribution measurements of particles formed during plasma chemical vapor deposition (CVD) of amorphous SiO_2 thin films using the LPDMA system [17]. The DMA-measured particle size distribution is in close agreement with that obtained from the electron microscopy images of the particles collected inside the plasma CVD reactor [Fig. 6 (a)]. It is possible for the LPDMA to continuously monitor the time evolution of particle size distribution during the plasma CVD reaction, as shown in Fig. 6 (b).

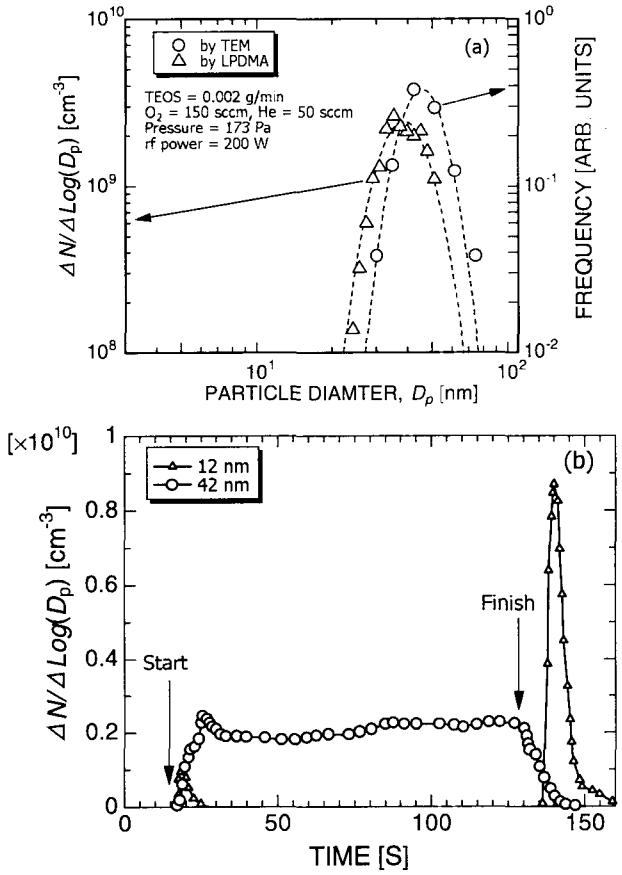

Fig. 6 Size distribution measurement of particles formed during PECVD of a SiO_2 film (a) and time evolution of particle size distribution along the PECVD reaction (b).

3. Calibration of DMA in a cluster-size range

The particle diffusion effects on DMA classification resolution can be suppressed utmost by using optimum L, which is 1 or 2 times the distance of R_2-R_1 and by increasing Q_{sh} to its limit [12]. Under these conditions, the DMA is applicable to the measurement of clusters with the minimum size around 1 nm. In comparison with the time-of-flight (TOF) mass spectroscopy, the DMA can supply high-resolution measurements even for clusters having high mass. In order to calibrate DMA results, standard monodisperse clusters with a known size are required. Recently, a new DMA calibration method using C_{60} monomer clusters dispersed in a gas phase has been suggested [7]. It is known that a C_{60} fullerene obtained by evaporation of a highly pure C_{60} powder at low pressures is of a form of an inherently monodispersed spherical cluster 1 nm in diameter. Fig. 7 shows the electrical mobility distribution of C_{60} monomer particles measured by a DMA [7]. From this, the diameter of the particles is estimated to be approximately 1.38 nm. This corresponds to the sum of the size of the C_{60} monomer (= 1 nm) and that of the sheath gas molecule (Ar; D_p = 0.38 nm). Furthermore, the width of the mobility distribution is in close agreement with the value calculated using the theory regarding DMA resolution.

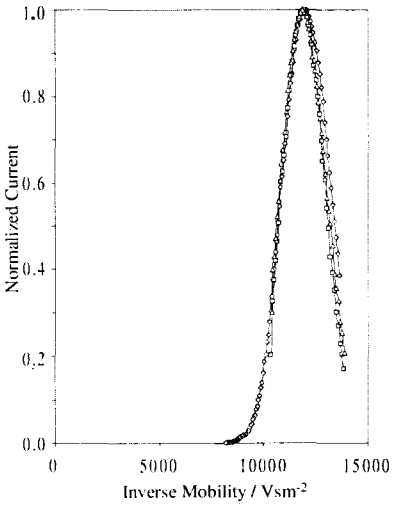

Fig. 7 Electrical mobility distribution of C_{60} monomers measured by a DMA.

4. Applications of DMAs

In general, characteristics of nanoparticles significantly depend on D_p. For example, the band gap of a semiconductor increases with a decrease in the particle size due to the quantum confinement effect. Ferromagnetic nanoparticles smaller than a critical size possess a single domain structure leading to magnetic properties superior to those of bulk materials. For better understanding of these size-dependent properties, research using size-classified nanoparticles is of critical importance. The above-mentioned size-classification ability of DMAs is appropriate to such research. One example is that size-classified monodisperse nanoparticles of a III-V compound semiconductor were synthesized by a gas phase reaction of monodisperse III-group metal (such as Ga and In) nanoparticles prepared by a DMA with vapor of a V-group

element (such as As and P) [18]. In another example, GaAs nanowires were synthesized using monodisperse gold nanoparticles as a catalyst [19], in which a DMA was used for size-classification of the nanoparticles in order to control the diameter of nanowires. Furthermore, a laser ablation technology in combination with a LPDMA was employed for the synthesis of monodisperse silicon nanoparticles [20, 21]. For devices using quantum dots such as a laser diode and a single electron transistor, use of size-controlled nanoparticles would be important. Lastly, research done by the authors is briefly described. Fig. 8 shows a transmission electron microscopy image of monodisperse lead zirconate titanate (PZT) nanoparticles that were produced by laser ablation followed by on-line thermal treatment. The particle size was classified at 7 nm with a LPDMA [22]. The inset of Fig. 8 shows the electron diffraction pattern of the nanoparticles, which clearly proves that the PZT nanoparticles possess a perovskite structure. The perovskite-structured PZT bulk is a ferroelectric material. If ferroelectricity is confirmed in the PZT nanoparticles, it becomes possible to fabricate high-density memory devices using the nanoparticles where a single nanoparticle acts as a single bit memory.

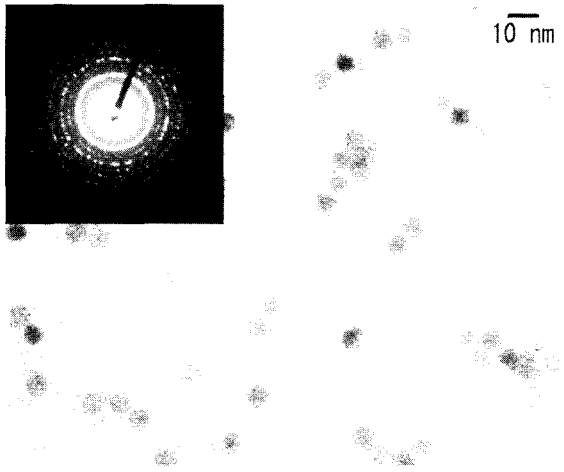

Fig. 8 A transmission electron microscopy image of monodisperse PZT nanoparticles 7 nm in diameter (inset: their electron diffraction pattern).

5. Summary

In accordance with recent progress of nanotechnologies, development of precise and dependable methods for measurement and classification of the size of nanoparticles have become of prime importance. The DMA technique introduced in this review, which is very appropriate for this purpose, is being developed by various research groups including the RIKEN-Waseda group to which the authors are affiliated. Presently, the DMA has the capability to classify nanoparticles with a size as small as 1 nm at a pressure range of approximately 0.1-100 kPa. This achievement has been contributing to the investigation of the physics of nanoparticles as well as their applications.

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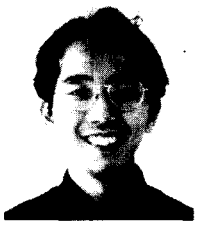

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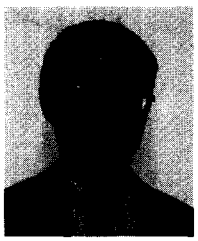

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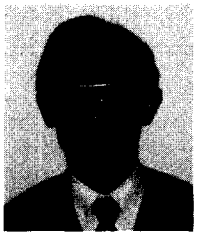

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