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Size measurements of standard nanoparticles using metrological atomic force microscope and evaluation of their uncertainties

Ichiko Misumi*, Kentaro Sugawara, Keiji Takahata, Kayori Takahashi, Kensei Ehara

National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), Central 3 bldg., 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563 Japan

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ABSTRACT

Size measurement methods for particles fixed on a substrate become increasingly important especially in the semiconductor industry, in addition to the conventional methods to measure particle size in the gaseous and liquid phases. In this study, size of standard nanoparticles (polystyrene latex (PSL), gold and silver) was measured using the metrological atomic force microscope (AFM) and its uncertainty was evaluated. Particle deformations were calculated based on the assumption of plastic deformation between particles and a substrate, and uncertainties derived from the particle deformation were also evaluated. Furthermore, the above-mentioned metrological AFM measurement results were compared with those obtained by other microscopies, such as SEM equipped with laser interferometer and AFM calibrated by standard samples, and were compared also with nominal values.

1. Introduction

In the field of semiconductor device manufacturing, pattern sizes become smaller, the device structures are changing from two dimensions to three dimensions, and accordingly strict quality control of contaminations and defects on semiconductor substrates are increasingly required these days [1]. Standard nanoparticles fixed on a silicon wafer come to be used as the reference standards in order to improve reliability of contamination and defect inspection apparatuses [2].

Size of the standard nanoparticles is generally measured in air or in liquid by using such a measurement method as differential electrical mobility analysis (DMA) [3,4] and dynamic light scattering (DLS) [5]. In general, the standard nanoparticles whose values are assigned by DMA or DLS are commercially available in the form of suspension [6]. The standard nanoparticles in suspension are widely adopted partly because their prices are relatively low compared with those standard nanoparticles which are fixed on a substrate and partly because users can put them on any substrates of their choice. It is not well known, however, that particle sizes are dependent on the measurement methods [7,8]. It becomes important to define the relation between the certified size of the standard nanoparticles in suspension and the size of the standard nanoparticles which are taken from the same suspension and fixed on a substrate.

Several types of microscopies can be used to measure size of the nanoparticles fixed on a substrate; e.g. scanning electron microscopy (SEM) [9], atomic force microscopy (AFM) [10], electron tomography [11] and transmission electron microscopy (TEM) [12]. In this study, the authors have focused on the AFM method. The AFM features several advantages, compared with the other microscopies, in measuring size of the nanoparticles; e.g. the AFM can be used in air and it can handle many types of materials. When higher level of accuracy is required in the measurement of nanoparticle size, commercially-available AFM instruments are often calibrated with the pitch standard, the step-height standard and/or the step pyramid-shaped standard [13,14]. Measurement time of the commercially-available AFM instruments has been improved and these instruments are useful for those users who want to know particle size distributions with bimodal and/or multimodal peaks. However, the commercially available AFM instruments calibrated with standard samples have a few disadvantages; e.g. 1) another hierarchy level is added in the traceability system to the length standard, compared with AFMs equipped with laser interferometers (metrological AFMs) [15,16], which could increase uncertainty derived from calibration of instruments, and 2) size measurement results of nanoparticles would have bias if the instruments cannot be calibrated appropriately with standard samples.

For many years, the authors have used the metrological AFM [17] for calibration of several types of standard samples including pitches of one- and two-dimensional gratings [17,18], step-height [19], profile surface roughness [20] and sizes of polystyrene latex (PSL) standard particles [10]. In the previous study [10], the authors proposed the

* Corresponding author.
E-mail address: misumi.i@aist.go.jp (I. Misumi).

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extended gravity center method to measure lateral particle diameter and calculated particle deformation caused by particle-substrate contact based on the assumption of elastic deformation [21] and the material property of thin film. It was difficult, however, to select suitable material properties of nano-material in the elastic deformation models, and therefore it is found necessary to investigate different deformation models.

The Maugius-Pollock model (the MP Model), a plastic model, has been adopted in this study [22]. This is a proven model as it has been applied successfully to the PSL and aluminum particle size metrologies using SEM. The strength of this model is that material properties of bulk materials can be used directly [23–25]. In order to minimize particle deformation caused by the contact of AFM tip, contact force (setting point) is set at the minimum necessary level to obtain AFM images. The authors measure the size of not only PSL nanoparticles but also gold and silver nanoparticles in this study. The PSL standard nanoparticles are the most common standard particles since they feature the highest sphericity among standard nanoparticles and their size distributions are narrow. The gold nanoparticles are stable and the smallest standard nanoparticles are commercially available. The silver nanoparticles are used in a wide range of applications, such as biosensors, antibacterial items, conductive inks and Raman scattering. In this paper, the authors will firstly report size measurement results obtained by using the metrological AFM and their uncertainty evaluation results for several types of standard nanoparticles. Next, this paper will present the calculation of particle deformations based on the assumption of plastic deformation between particles and a substrate and the evaluation of uncertainties derived from the particle deformation. Furthermore, this paper will report the comparison results between the metrological AFM and other microscopies such as SEM equipped with laser interferometer and AFM calibrated by standard samples, as well as between the metrological AFM and nominal values. Finally, the authors will identify the future challenges in the particle size measurements using AFMs.

2. Definitions of particle size

Measurand in this study is the number average diameter of spherical particles. When the particles are subject to deformation due to the particle-substrate interaction, this study focuses on spherical particles before the particles deposit on the substrate. In this study, two types of particle sizes which have been often used in the AFM measurement are defined [26].

The first type of particle size is defined as particle diameter in the height direction, the distance between surface of a substrate and top of a particle, D_H. Fig. 1 shows the conceptual diagram of the particle diameter in the height direction [27]. The advantage of measurements of particle diameters in the height direction is that this method can be applied to several types of nanoparticles for which some base plane area and isolated and/or single layer particles can be obtained in an AFM image.

The other is lateral diameter, which is defined as distance between center points of neighboring two particles, D_L (Fig. 2(a) [27]). In the case of the conventional AFMs, since the position of an AFM scanner is controlled just in the Z-axis direction, AFM profile information in the height direction is reliable but reliability of AFM profiles around sidewall of particles is not high even after deconvolution of AFM tip shapes. In order to compensate for this limitation, the characteristic of standard nanoparticles with high sphericity and high size-uniformity to form close-packed structure relatively easily is often used. The advantage of this definition is that lateral diameters can be obtained without using AFM profiles around sidewall of particles. The disadvantage of this method is that it is difficult to evaluate 1) deformation induced by the interaction of neighboring particles and 2) air gap generated when diameter is different between neighboring particles [22]. In the previous paper, the extended gravity center method (GCM) was proposed as a method to calculate lateral diameter [10]. The extended GCM method is also used in this study (Fig. 2(b) [10]).

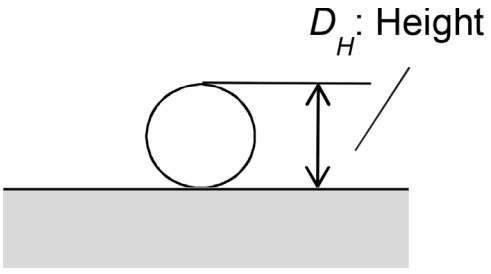

Fig. 1. Definition of particle diameter in the height direction, D_H [27].

In this study, both the diameter in the height direction and the lateral diameter are measured for PSL nanoparticles since close-packed structure is expected to be formed while diameter in the height direction alone is measured for gold and silver nanoparticles since close-packed structure is hard to be formed.

3. Measurement conditions

Table 1 shows the measurement conditions adopted in this study. Gold 10 nm, Silver 20 nm, PSL 30 nm, PSL 100 nm and PSL 300 nm are the standard nanoparticles measured in this study, whose nominal diameters are 10 nm, 20 nm, 30 nm, 100 nm and 300 nm, respectively. Sample preparation procedures are designed by referring to the technical protocols of the comparative measurements in the US [27] and the on-going comparative measurement in Asia Pacific Metrology Program (APMP) [28]. The authors are participating in the APMP comparison as co-pilot laboratory members. The sample is prepared in a clean room (class 10000). The air temperature and the relative humidity of the clean room are kept at 20 ° Celsius and 50% throughout a year. Cleaved mica is used as a substrate. There are a couple of advantages in using mica substrates: 1) flat surface at the atomic level is obtained and 2) monolayer structure of particles is formed relatively easily since the mica substrate surface is highly wettable to allow a drop of diluted solution to spread widely. In an attempt to determine optimum sample preparation conditions to obtain the best AFM images for particle diameter calculation, several diluted particle suspension solutions with varied density were prepared and each of the solutions was dropped onto mica substrate. The samples were dried in the clean room and drying time was approximately twenty-four hours. These samples were investigated with laser confocal microscopy and test measurements by using AFM were performed. Table 1 shows the selected sample preparation conditions. As shown in Table 1, scanning ranges are varied, depending on the sample types, because the ranges are specified in a way to match the positions of particles fixed on substrates. The number of frames is specified in a way to obtain sufficient AFM images of more than 100 particles.

The detailed information on the metrological AFM is presented elsewhere [17]. The metrological AFM is equipped with high-resolution laser interferometers on its XYZ axes and it is traceable to the length standard. The AFM cantilever probes used in this study are manufactured by Olympus Corporation (OMCL-AC160TS), featuring resonant frequency of approximately 300 kHz and spring constant of about 42 N/m. The tip is symmetric when it is viewed from the front end of a cantilever. Scanning direction is almost perpendicular to the cantilever axis. AFM measurement mode is the AC mode (the intermittent contact mode). The AFM is installed in a clean room (class 10000). The air temperature and the relative humidity of the clean room are kept at 20 ° Celsius and 50% throughout a year.

The smallest possible contact force (setting point) to allow AFM images to be obtained is selected in order to minimize particle deformation due to contact of the AFM tip. In the case of the PSL particles, for instance, setting point was set at between about 0.96 and 0.97 when the free vibration amplitude of the cantilever was 1. When the setting