Topics

Pre-standardization study for guidelines for shape and size quantitative analysis of nanoparticles by atomic force microscopy

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The global production and distribution of industrial nanoparticles is expanding as nanotechnology advances in new material applications. Precise design and control of nanoparticle size and shape are critical to the performance of industrial nanoproducts. Atomic force microscopy (AFM) is a surface chemical analysis technique that enables nanoscale measurement of topography on material surfaces. The objective of the RRT project conducted within the VAMAS (Versailles Project on Advanced Materials and Standards) TWA 2 (Surface Chemical Analysis) is to establish practical guidelines for quantitative measurement and analysis to determine the size and shape of nanoparticles. Furthermore, we are aiming for international standardization in ISO (International Organization for Standardization) TC 201 (Surface Chemical Analysis). Here we present the progress of the pre-standardization research project (Guidelines for shape and size analysis of nano-particles by AFM, Project A24) in VAMAS/TWA 2.

1. Introduction

VAMAS stands for Versailles Project on Advanced Materials and Standards. It is one of the international cooperation projects agreed upon at the G7 Economic Summit held in Versailles, France in 1982. Initially, the participating members were the G7 nations and the EU, but in 2007, the number of participating countries was expanded to include Taiwan, South Korea, India, Australia, Mexico, China, and other emerging countries. Its purpose is to provide a technical basis for harmonized measurement methods, to promote innovation and commercialization of advanced materials through international cooperation leading to standards, and to facilitate world trade. TWA 2 (surface chemical analysis), which has existed in the technical working area since its inception, is an organization that conducts pre-standardization studies on surface chemical analysis methods. It is promoting pre-standardization research through round-robin tests (RRT) for inter-laboratory comparison. TWA 2 has four areas: mass spectrometry, scanning probe microscopy (SPM), electron spectroscopy, and data-driven metrology.

Now, as the application of nanotechnology to new materials progresses, the global use of nanobjects, especially industrial nanoparticles (manufactured nanoparticles), is rapidly expanding in the industrial sector. Precise design and control of nanoparticle size and shape are critical to the performance of industrial nanoproducts. Implementing a quality control system for nanoparticle production requires information on dimensional parameters that characterize the population. However, international standards for quantitative characterization of size, shape, and size distribution at the nanoscale have not yet been developed. Therefore, standardization of topographic quantitative evaluation protocols in real space is needed to facilitate the industrial production of nanoparticles. Such information on dimensions also needs to be standardized in view of potential risks associated with nanoparticles to the environment, health, and safety (EHS).[1)]

Nanometrology is the science of measurement and characterization at the nanoscale. Atomic force microscopy (AFM) is a leading nanometric method for visualizing the three-dimensional shape of nanoparticles. Quantitative evaluation methods for nanoparticle shape and size by AFM are sought by researchers and engineers in academia and industry.[2)] One of the artifacts in AFM shape imaging is due to the finite size of AFM tips used for surface scanning. Therefore, there is a great need for establishing guidelines for quantitative AFM measurements and correction methods to extract the true size and shape of nanoparticles as an

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international standard.

This paper describes the progress of the pre-standardization research project in VAMAS/TWA 2 for the establishment of guidelines for shape and size analysis of nanoparticles by AFM (Project A24). Figure 1 shows the public call flyer for participating institutions at the start of this project. Ten institutions from Northeast Asia, Europe, North America, and Oceania participated in this project.

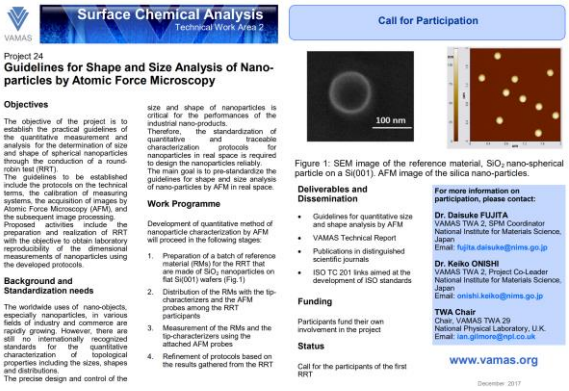


Fig 1. VAMAS/TWA 2 Project A24 familiarization.

2. Project objectives

The objective is to establish the guidelines for quantitative analysis to determine the size and shape of spherical nanoparticles through RRT. The guidelines to be developed will include protocols for terminology, calibration of the measurement system, image acquisition by AFM, and subsequent image processing. The design and preparation of RRT were implemented so that laboratory reproducibility of nanoparticle dimensional measurements could be obtained using the proposed protocol. The development of a quantitative method for nanoparticle characterization by AFM proceeded through the following steps.

(1) Preparation of RRT reference materials (RMs)
(2) Distribution of tip characterizers, probes, and RMs
(3) Measurement of RMs and tip characterizers
(4) Improve protocols based on results collected

3. Sample sets of round-robin tests

This RRT will establish a standard procedure for quantitative evaluation of the size, shape, and size distribution of monodisperse spherical nanoparticles on planar substrates by AFM. RRT participants will receive a complete sample set of AFM probes, probe-tip characterizers, and reference materials

【AFM probes】

Cantilever probes with Al reflective coating were stored in a container box as shown in Figure 2. The two types of probes are NCHR (NanoWorld) and OMCL-AC160TS (Olympus), which are designed for non-contact or intermittent contact mode and made from highly doped monolithic Si to dissipate electrostatic charges. The typical value of the radius of curvature of the NCHR probe-tip is 8 nm and that of the OMCL one is 7 nm.

【Probe-tip characterizer】

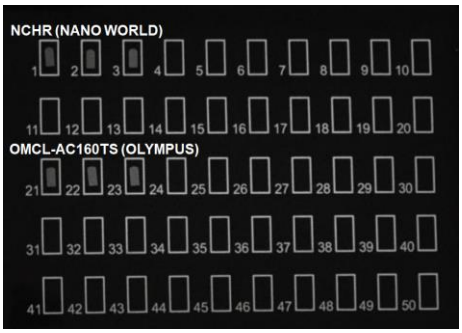


Fig 2. Container box containing AFM probes.

A commercially available tip characterizer PA01 (MikroMasch) was prepared for the evaluation of probe-tip geometry used in RRT. PA01 has a hard, sharp pyramidal nanostructure and is used as a sample for tip-shape characterization. Pyramid-shaped nanostructures have a base length of 50-100 nm and a height of 50-150 nm. The radius of curvature of the sharpest apex is less than 5 nm. SEM image of the tip characterizer is shown in Figure 3.

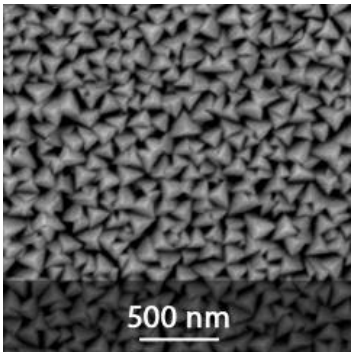


Fig 3. SEM image of probe characterizer.

【Nanoparticle reference materials】

The reference material selected for the analysis of nanoparticle shape and size was spherical silica (SiO_2)

nanoparticles with an average diameter of 113 nm (provided by AIST, Japan) dispersed on an atomically flat Si(100) wafer. The particle size distribution measured by the Scanning Mobility Particle Sizer Spectrometer (SMPS) is shown in Figure 4. The particles are monodisperse with well-defined diameters. Spherical silica nanoparticles were selected for their higher stability, chemical inertness, and mechanical robustness compared to other spherical nanoparticles such as polystyrene and gold.

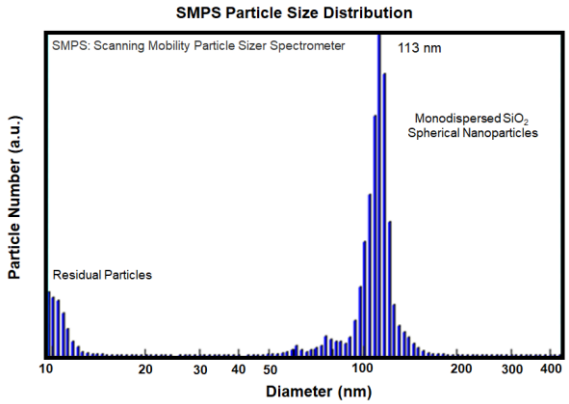


Fig 4. Diameter distribution of spherical SiO_2 nanoparticle standards.

4. Measurement procedure for round-robin testing

【Calibration of measurement systems】

It is recommended that the X-, Y-, and Z-axis scanners in the AFM system should be properly calibrated at regular intervals using certified reference materials (CRMs). A typical example of height calibration is shown in Figure 5.

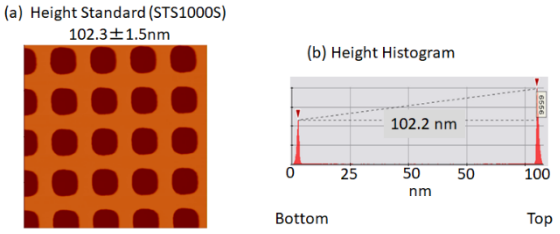


Fig 5. Z-axis calibration of AFM measurement systems using height standards.

【Evaluation of probe tip shape】

The cantilever probe-tip shall be mounted on the AFM tip holder and the tip characterizer (PA01) shall be set horizontally on the sample holder. Use the system's optical microscope to properly position the probe-tip in the active area of the PA01. The measurement shall be started at a time when the thermal drift can be considered negligibly small. It is recommended to wait typically at least 1 hour after setting the sample in the AFM system.

The measurement mode shall be intermittent contact or non-contact mode. The signals recorded are the topography or height signal and the error signal (the difference between the set value and the measured one). Scanning parameters such as set point, gain, and scanning rate shall be optimized to minimize the error signal. It is recommended that the error signal should be less than 2 nm after optimization.

The AFM scanning range of the PA01 tip characterizer should be set to 1000 nm × 1000 nm and the pixel size to 512 × 512. The corresponding pixel spacing is about 2 nm (≅ 1000 nm/512). A typical AFM topographic image and its error signal image of PA01 measured in non-contact mode are shown in Figure 6.

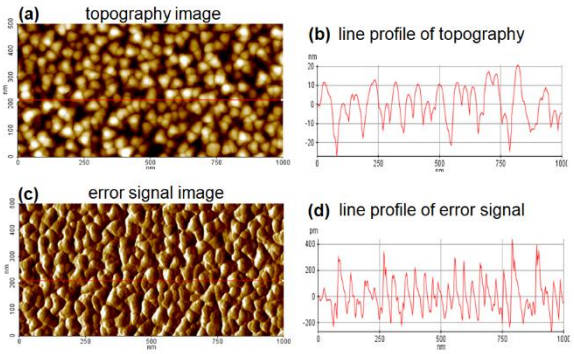


Fig 6. (a) AFM Topographic image of PA01. (b) Typical line profile of topography image. (c) Associated error signal image. (d) Specific line profile of error signal image.

【Measurement of reference materials】

The AFM scanning range for the topography and error signal should be set to 3000 nm × 3000 nm and the pixel size to 1024 × 1024. Pixel spacing is about 3 nm (≅ 3000 nm/1024). The fast and slow scanning directions are set in the X and Y axes, respectively. Store raw data of height and error signals. Error signal data can be analyzed to estimate distortions that suboptimal scanning parameters may cause. A typical error signal image of a nanoparticle reference material measured in non-contact mode is shown in Figure 7. It can be seen that the error signal is maintained at approximately less than 2 nm.

【Measurement data processing】

Two types of analysis are used to extract information about the size and shape of nanoparticles. One is the measurement of the heights and diameters of nanoparticles to extract information on size and its distribution. The other is an analytical method that reconstructs the topographic image using the probe-tip shape extracted by blind tip reconstruction.[3,4)]

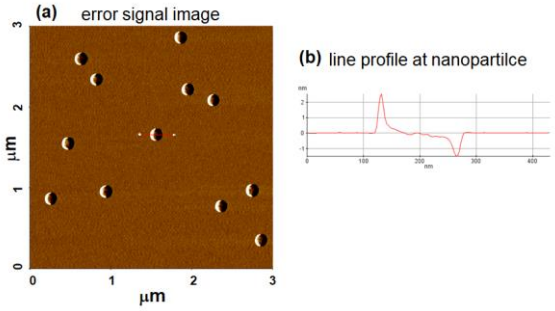


Fig 7. (a) AFM error signal image of spherical nanoparticles standards. (b) A line profile of the error signal at a nanoparticle.

（1）Height analysis of nanoparticles：

First, the appropriate plane correction process is applied to the raw AFM topographic image data of the RMs, if necessary. The height of each nanoparticle is then measured by a line profile along the fast scanning direction, including the highest points of the individual nanoparticles, as shown in Figure 8. Measure all nanoparticles in the AFM image.

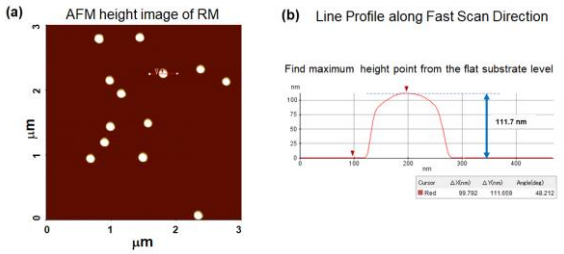


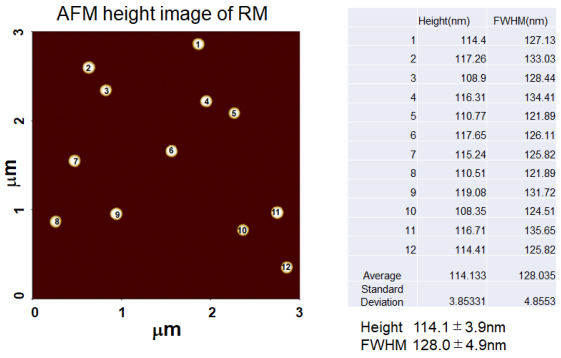
Fig 8. (a) AFM topographic image of spherical nanoparticles. (b) Particle height measurement by line profile.

（2）Nanoparticle diameter analysis:

The raw data of the nanoparticle topographic image shall be subjected to appropriate plane correction processing as needed. The full width at half maximum (FWHM) shall be measured, which corresponds to the apparent diameter of each nanoparticle, by the appropriate line profile along the fast scanning direction, as shown in Figure 8. It should be noted that the measured FWHM value does not represent the actual diameter. The blurring artifact is caused by the finite size of the probe-tip, which can be called "dilation" in mathematical morphology. All individual nanoparticles in the image must be measured.

（3）Extracting means and standard deviations：

After measuring the geometric quantities of all nanoparticles by appropriate line profiling, the mean and standard deviation values of the height and width of the measured spherical nanoparticles are extracted, as shown in Figure 9.



	Height(nm)	FWHM(nm)
1	114.4	127.13
2	117.26	133.03
3	108.9	128.44
4	116.31	134.41
5	110.77	121.89
6	117.65	126.11
7	115.24	125.82
8	110.51	121.89
9	119.08	131.72
10	108.35	124.51
11	116.71	135.65
12	114.41	125.82
Average	114.133	128.035
Standard Deviation	3.85331	4.8553

Fig 9. AFM topographic image of spherical silica nanoparticles (left), and extraction of mean and standard deviation values of height and width (right).

5. Round-robin test results

【AFM measurement of a large number of nanoparticles】

At NIMS, the size distribution of spherical silica nanoparticles of 100 nm diameter class dispersed on Si(100) wafers used in this RRT was separately measured by AFM, and the results are presented. The results of height measurements of a large number of 1032 spherical silica nanoparticles to obtain sufficient statistical certainty are shown in Figure 10. NX-10 (Park Systems) was used as the AFM system, and NCHR was used as the probe. Topography image measurement was performed using the non-contact mode of the AM method. The average height of the measured spherical silica nanoparticles was 114.07

nm, in very good agreement with the average diameter (113 nm) measured by the scanning electric mobility particle sizer (SMPS). As for the size distribution of spherical silica nanoparticles, the distribution is almost normal, and the standard deviation is sufficiently small at 3.41 nm. This result indicates that the nanoparticles are mono-disperse with a very good size uniformity.

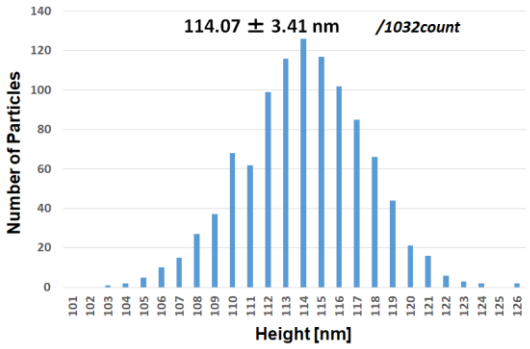


Fig. 10. Height distribution of silica nanoparticle standards (based on non-contact AFM measurements of 1032 nanoparticles).

【RRT: Spherical nanoparticle height measurement】

The following are the results of compiling the data reported by the RRT participating institutions. Figure 11 shows a histogram of all reported height data for 113 spherical silica nanoparticles using the NCHR probes, which are all added together. It was basically normally distributed, with a mean of 114.2 nm and a standard deviation (σ) of 4.2 nm. This result is in very good agreement with the mean particle size from SMPS measurements (113 nm) and the mean particle height from AFM multiple measurements (114 nm).

All reported height data for 118 silica nanoparticles using the other distribution probe, the OMCL probe, were added together and displayed as a histogram in Figure 12. In the case of the OMCL probe, the dispersion of the particle height was also normally distributed, with a mean value of 115.1 nm and a standard deviation of 4.1 nm. The results here are in good agreement with the average particle size from SMPS measurements and the average of many measurements of particle height from AFM.

These RRT results indicate that in the case of size evaluation of spherical nanoparticles by AFM topography measurements, the nanoparticle height measurements can be considered as nanoparticle diameter measurements.

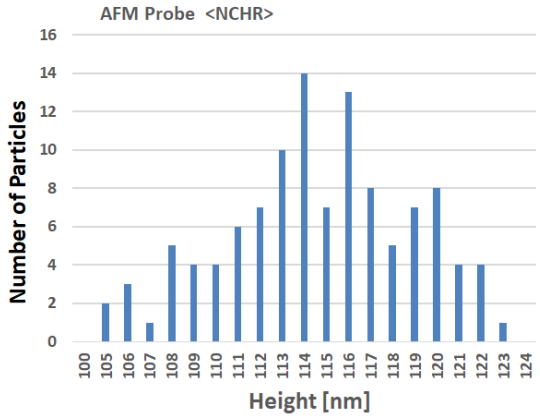


Fig 11. Height distribution of silica nanoparticles by summing all reported values of RRT using NCHR.

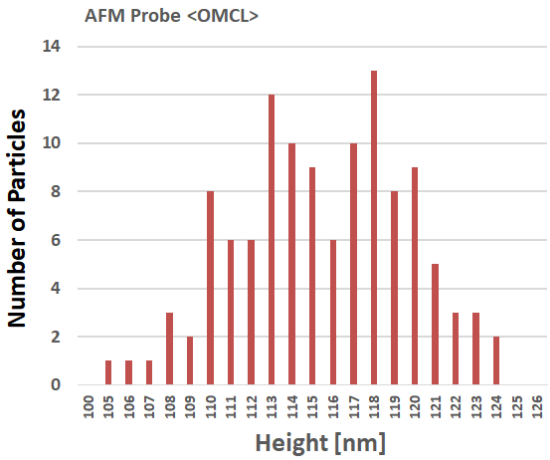


Fig 12. Height distribution of silica nanoparticles by summing all reported values of RRT using OMCL.

【RRT: Spherical nanoparticle FWHM measurement】

The mean values and standard deviation for the height and FWHM of spherical silica nanoparticles reported by the participating institutions in RRT for AFM topographic measurements using the NCHR probes are summarized in Table 1. As can be seen at a glance, the FWHM values of spherical silica nanoparticles determined by AFM are larger than the nanoparticle height values. The standard deviations, which correspond to variability, were similar to those of the nanoparticle heights. However, the FWHM values, which correspond to the apparent diameters of the particles, were about 15% larger. These results indicate that in the evaluation of nanoparticle size by AFM, the

measured value in the horizontal direction, which corresponds to the width, is excessive due to the dilation effect caused by the probe-tip shape. Therefore, it indicates that sufficient care should be taken in handling dimension data in the horizontal direction.

【Correction of spherical nanoparticle FWHM values】

In order to correct for the overestimation in the apparent AFM transverse width measurement described above, it is necessary to correctly assess the shape of the AFM probe-tip used for the measurement, in particular the value of the tip curvature radius. The RRT participating organizations were asked to report the values of the tip radius of curvature of the AFM probe-tips they used for the measurements of the tip characterizers. The mean value of the curvature radius of the NCHR probe-tips measured by the PA01 was 12.0 nm with a standard deviation of 3.5 nm. The corrected FWHM value was approximately 110 nm, slightly underestimating the actual particle size, assuming a tip curvature radius of 12 nm for the NCHR probe. This is due to the fact that the radius of curvature of the sharpest vertex of the PA01 used for the RRT is about 5 nm. The estimated curvature radius values include the dilation effect due to the tip curvature radius of the nanoscale projections of the tip characterizers. It should be noted that this makes the estimate slightly overestimated than the actual.

Therefore, additional measurements were carried out on the NCHR probes using the 70 nm line-width standard NCDM-70X (VLSI Standards, Inc.), which is usually used in semiconductor microfabrication evaluation. Since it is equipped with an even steeper radius of curvature at the edges, its line profile can be used as a probe-tip characterizer (see Figure 13).

Reported values for height and FWHM (NCHR probe)

#	Institution	Nanoparticle Height (nm)	Nanoparticle FWHM (nm)
1	A	114.1±4.0	125.9±2.1
2	B	114.1±3.9	135.4±4.3
3	C	111.5±4.4	134.9±4.1
4	D	113.0±7.8	115.6±11.2
5	E	113.4±4.3	127.3±4.2
6	F	113.0±4.2	142.2±5.7
7	G	114.3±2.7	121.5±2.7
8	H	116.0±2.7	151.9±3.9
9	I	117.9±3.5	124.3±2.3
		114.1 ± 4.2 nm	131.0 ± 4.5 nm

Table 1. Reported nanoparticle height and FWHM from RRT.

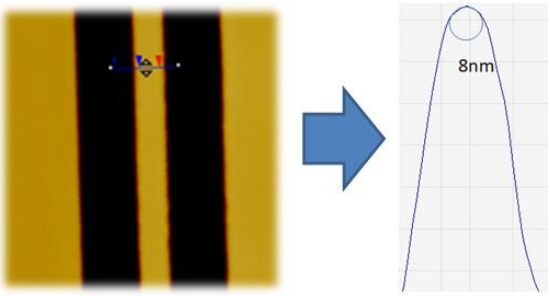


Fig 13. Evaluation of the tip curvature radius of the probe-tip using the NCDM-70X.

The NCDM-70X linewidth standard is a very precise semiconductor microfabricated trench structure with extremely sharp edges at both ends of the linewidth standard. AFM topography measurements can be performed orthogonally to the line width sample, and the tip radius of curvature can be evaluated by removing the line width equivalent from the line profile and extracting the tip cross-sectional profile by conjunction. The tip radius of curvature of the NCHR probes used in this way was evaluated, with a mean value of 10.1 nm and a standard deviation of 3.2 nm.

Assuming a tip curvature radius of 10.1 nm for the NCHR probe, a corrected FWHM value of 113.9 nm and a standard deviation of 8.8 nm were obtained from this result (see Figure. 14). The corrected FWHM values are in very good agreement with the SMPS particle size measurement of 113 nm for monodisperse spherical silica nanoparticles and the average value of 114 nm in the AFM height measurement RRT, a difference of less than 1%.

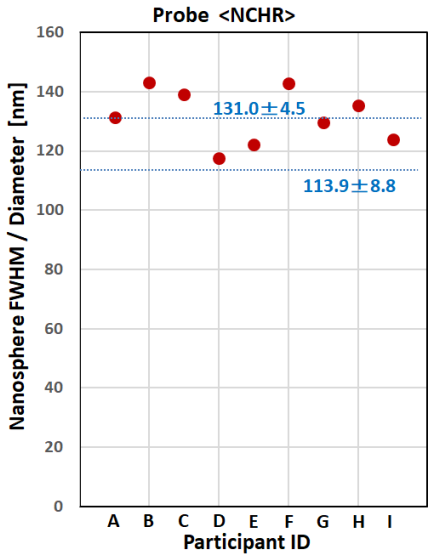


Fig 14. FWHM measured and corrected mean and standard deviation.

6. Summary and future prospects

A pre-standardization study was conducted to establish guidelines for quantitative analysis of nanoparticle size by AFM topography measurement. A round-robin test was performed using a reference material consisting of spherical silica nanoparticles of uniform particle size dispersed on the surface of a Si wafer. The nanoparticle height measurements showed good agreement with the nominal particle size. On the other hand, the FWHM measurement showed deviations due to the dilation effect of the tip shape, but good agreement with the nominal particle size was obtained by correcting the tip curvature radius.

Based on the knowledge of the procedures for nanoparticle size quantification by AFM obtained in the international joint RRT in VAMAS/TWA 2, the next step is to submit a new work item proposal (NP) as an international standard in ISO/TC 201/SC 9 (scanning probe microscopy).

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