

Recent trends in pre-standardization research and international standardization in quantitative surface nanostructure analysis using scanning probe microscopy

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Scanning probe microscopy (SPM), such as atomic force microscopy (AFM), is a surface chemical analysis technique that can measure the shape, physical properties, and function of material surfaces at the nanoscale. The international standardization process for SPM nanoscale analysis consists of two stages: VAMAS (Versailles Project on New Materials and Standards), which is in charge of pre-standardization, and ISO (International Organization for Standardization), which is in charge of international standardization. In the corresponding ISO/TC201 (Surface Chemical Analysis), SC9 is working on the international standards of SPM. In this paper, the author will introduce the recent progress of the pre-standardization/international standardization project on nanoscale shape analysis using AFM, which the author is promoting as a project leader in VAMAS and ISO.

1. Introduction

TWA2 (surface chemical analysis) is the most active technical working area (TWA) of VAMAS from its inception in 1982 to the present¹⁾. In the VAMAS/TWA2, international joint projects on pre-standardization of quantitiveness, sensitivity, resolution, etc. of surface chemical analysis methods are conducted through the round robin test (RRT) among participating research institutes.

Since there is a wide range of surface chemical analysis methods, there are four program areas according to their characteristics as measurement methods: (1) mass spectrometry, (2) scanning probe microscopy, (3) electron and optical spectroscopy, and (4) data-driven measurement methods (data workflow, methods, and best practices). The author is currently chairing the SPM and Data Workflow program areas.

In ISO / TC201 (surface chemical analysis), SC9 was established in 2004 as a sub-committee (SC) in charge of SPM technology²⁾. SPM is a microscopic measurement method that is surface-sensitive and enables multidimensional characterization of physical and chemical properties. For this reason, the international standardization

of SPM is positioned to be promoted by the scheme of TC201 as one of the surface chemical analysis methods. The author is the representative director of JSCA, an ISO / TC201 domestic deliberation organization under the JISC (Japanese Industrial Standards Committee), and is the representative of the JISC delegation to the ISO/TC201 annual meeting.

In this paper, I will introduce quantitative nano-shape analysis by AFM, among the international standardization activities of SPM nano-measurement that I have been in charge of. Mainly the progress of pre-standardization research in VAMAS/TWA2/SPM and international standard development in ISO/TC201/SC9 (SPM) will be introduced.

2. Timeline of International Standardization of SPM

In the timeline for international standardization of SPM, the first work item to be tackled was the standardization of terminology used in SPM³⁾. The international standard has been published as ISO 18115 for the terminology such as SPM terms and abbreviations, contact mechanics terms and acronyms, and other related terms. The translation JIS for ISO 18115 was made mainly by JSCA's SPM experts, and was published as JIS K 0147-2 in 2017. Starting from the standardization of terminology, international standardization

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of SPM progresses in two different directions. One is the direction related to data management such as data formats that support the multidimensional measurements of SPM, information formats that enhance the independent availability of measurement data, and image processing that improves the quality of image data. The other is the direction of quantification in SPM measurements, such as the calibration methods for geometric dimension measurements, the calibration methods for the characterization of physical and chemical properties, and the certified reference materials required for the above calibrations. It is expected to facilitate the development of data processing programs that are unified with data exchangeability and contribute to the improvement of quantitiveness. The target to be aimed at in the standardization timeline is the construction of an SPM data platform that integrates the multidimensional big data processing environments created by SPM measurements and the cloud-based databases.

3. RRT for probe-shape correction of AFM images

The authors carried out the “International RRT for reproducible restoration methodology for AFM topography images using probe shape function” from 2012 to 2016 as a VAMAS / TWA2 A15 project. The purpose of this RRT project is to establish a method for correcting AFM topography images with good reproducibility by quantitatively measuring the probe shape function (PSF). When measuring the three-dimensional shape of the sample surface using AFM, the existence of image artifacts caused by the finite size of the probe tip and various shapes cannot

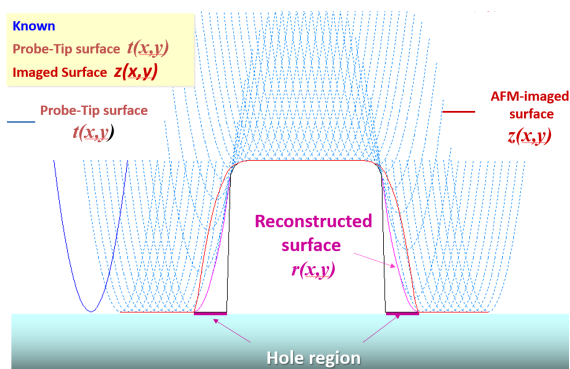


Figure 1: Probe shape effect and correction in AFM measurement.

be ignored (Fig. 1). When quantitative 3D surface shape measurement with nanoscale resolution is required, the guidelines for quantitatively measuring PSF and appropriately correcting the original image are indispensable. The AFM topography image can be expressed not by the convolution operation of the probe shape function but by the operation called dilation in mathematical morphology^{4,5}.

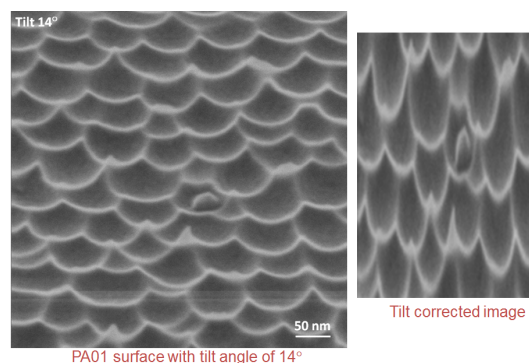


Figure 2: Helium ion microscopy image of porous alumina reference material (RM) for AFM tip shape evaluation.

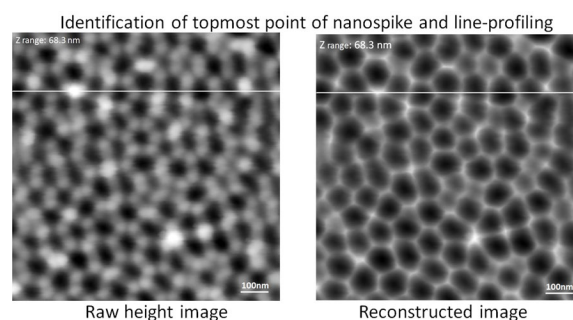


Figure 3: Topographic original image (left) and reconstructed image (right) of RM.

Validity test of image reconstruction - preservation of height information

The topography image $z(x, y)$ corresponds to the true surface profile image $s(x, y)$ dilated by the probe shape function $t(x, y)$. The topography image, including the part dilated by the probe shape, can be reconstructed as an approximate image $r(x, y)$ by an operation called erosion in mathematical morphology. The purpose of RRT is to obtain an approximate image using a sharp nanostructured reference material (RM) to extract the shape and size (radius

of curvature) of the probe and to evaluate the effectiveness of the AFM topography image reconstruction protocol. The RM used was porous alumina with a spike curvature of 2-3 nm, a septa thickness of less than 5 nm, a cell pitch of 100 ± 10 nm, and a pore depth of 40 ± 5 nm (Fig. 2). The standard value of the radius of curvature of the AFM tip (PPP-NCHR, NanoWorld) supplied to the RRT is 7 nm. The validity of the proposed protocol is verified by a proper estimation of the tip shape (comparison with FE-SEM imaging) and the validity of the image reconstruction (preservation of height information) as shown in Fig. 3.

As data preprocessing, simple tilt correction and noise reduction are performed as necessary. Comparison of height preservation of image reconstruction (erosion) shows that the relative deviation of height before and after erosion is negligibly small (ca 0.5%). Locally, the near-complete preservation of height information at the top apex was clearly shown. The PSF at the tip of the probe is extracted by blind reconstruction (BR). It is possible to extract the probe characteristic function (PCF) and tip radius of

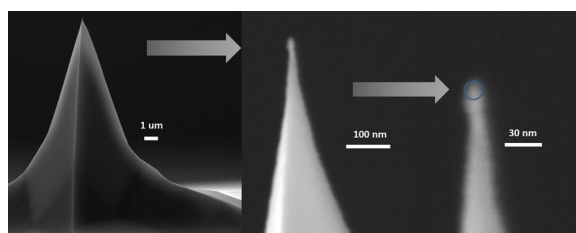


Figure 4: Estimation of tip radius of curvature by FE-SEM.

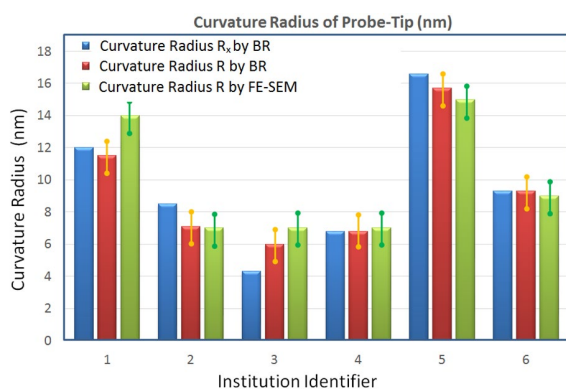


Figure 5: Test of proper probe shape (radius of curvature) estimation.

curvature from the PSF⁶). The radius of curvature at the tip can also be evaluated from the FE-SEM measurement after the AFM measurement (Fig. 4). The radius of curvature extracted by BR and the radius of curvature measured by FE-SEM showed good agreement (Fig. 5). These results show the usefulness of the proposed protocol.

The PCF is a quantitative index of the sharpness of the tip of the probe as well as the amount of probe characteristics such as radius of curvature and cone angle. In this way, by advancing the probe shape evaluation and image correction protocols and standardization of appropriate standard materials, it is possible to quantify the three-dimensional nanoscale surface shape measurement by AFM⁷). This RRT project has successfully demonstrated the effectiveness and usefulness of a protocol for quantitative evaluation of probe tip shape and image reconstruction using the probe shape in use.

4. ISO standardization for AFM image probe shape correction

Image correction using an accurate probe shape can contribute to the advancement of AFM critical dimension (CD) measurement, which quantitatively evaluates the dimensions and shape of nanodevices. Based on the technical report of the VAMAS / TWA 2 RRT project (A15: Reproducible restoration methodology for AFM topography images using probe shape function), international standardization in ISO was requested. From this point of view, the "Guideline for restoration procedure for AFM images diluted by finite probe size" was newly introduced at the SC9 subcommittee of the 2018 ISO / TC 201st Annual Meeting. A new work item proposal (NWIP) was made. It was proposed by JISC after demonstrating the effectiveness of the proposed protocol. This document provides guidelines for quantitative procedures for the restoration of topographic images measured by AFM. The AFM image contains image expansion artifacts due to the finite size and shape of the probe. This international standard includes quantitative characterization of the vertices of the AFM probe in use and restoration of AFM topography images using the actual probe shape. This standard is recommended for extracting the exact properties of the surface morphology of various nanoobjects, including nanoparticles, nanorods, two-dimensional materials, nanoelectronic devices, nanostructured materials, biomaterials, and more. This

standard is useful for a variety of industry research, development, manufacturing, and inspection users, as well as manufacturers of AFM equipment. An NP vote was held in 2019, and it was adopted as AWI by the majority in favor. A draft work was prepared in 2020 based on comments from experts (WD 23729). The contents of the work draft are shown in Fig. 6.

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Figure 6: Contents of ISO/WD 23729

This working draft (WD 23729) was reported to the SC9 subcommittee at the ISO/TC201 annual meeting held in September 2020 and was subsequently submitted for committee draft (CD) ballot. The author, as the project leader, will work with experts from various countries to brush up on the document for the DIS ballot.

5. Standardization of nanoparticle size measurement by AFM

As the commercialization of various nanoscale-sized nanoparticles progresses, there are increasing demands from industry and academia to quantitatively evaluate the size and shape characteristics of 100 nm-class nanoparticles using AFM. In response to these needs, "International round robin test for guidelines for shape and size analysis of nanoparticles by atomic force microscopy" was adopted as a proposal from NIMS from December 2017 as an A24 project of VAMAS/TWA2. Since then, the international RRT has started. As the standard material (RM), silica spherical nanoparticles (diameter: about 100 nm) arranged in a

monodisperse on a flat silicon substrate were used (Fig. 7). In 2020, we accepted several requests for additional participation in RRT from National Institutes of Metrology and Standards (NMI) such as Belgium and the Netherlands. The RM is close to a true sphere and has good and uniform size distribution characteristics. Participating agencies measure nanoparticle diameter, height, topographic images and probe shape data according to the protocol. Quantitative analysis using the probe tip shape in accordance with WD 23729 is underway and the analysis results shall be included in the technical report (TR). A TR that summarizes the analysis of international RRT results, including additional data, shall be reported in 2021.

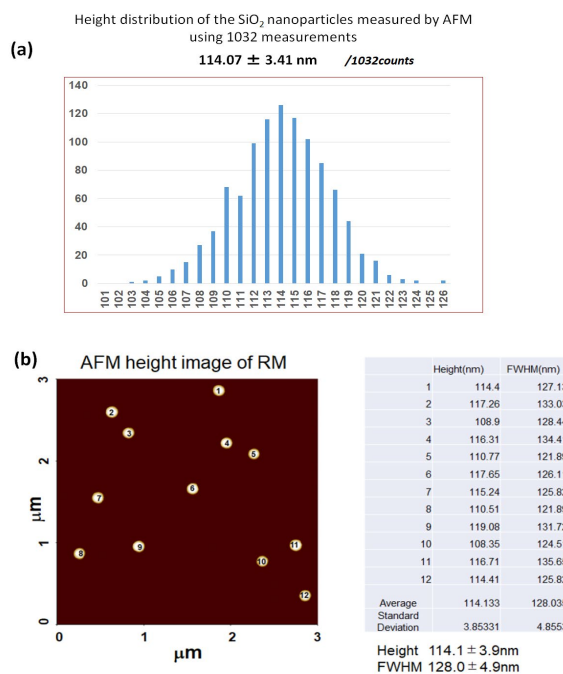


Figure 7: Measured size distribution of 100 nm class nanospherical particles used for RRT (a) and AFM measurement example (b).

6. Summary

In September 2020, the 29th General Assembly and Subcommittee Meetings of ISO/TC 201 were held as virtual meetings. At the SC9 subcommittee meeting, many proposals for new work items such as nanoparticle measurement and nanoscale potential measurement were

made from Japan. Japan's activities have been maintained in the standardization of advanced nanoscale measurement technologies such as SPM. In the future, standardization needs such as operando nanocharacterization and data-driven measurement corresponding to big data will become a trend.

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