Current standardization activities for the measurement and characterization of nanomaterials and structures

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Abstract. Current standardization activities relating to the measurement and characterization of nanomaterials and nanostructures are described. The working items relating to single-wall and multiwall carbon nanotubes, which have been discussed by WG2 of ISO TC229 on Nanotechnology, are explained together with the social requests for standardization and the scope and structure of ISO TC229. In addition, the standardization of AFM probe characterization, which is under discussion at ISO TC201 (Surface Chemical Analysis)/SC9 (Scanning Probe Microscopy), is introduced. A new type of probe characterizer necessary for the precise measurement of probe shape is described, and the merit and utility of a probe-shape function that gives the relation between the probe length and width are also explained.

1. Introduction
After the establishment of the National Nanotechnology Initiative (NNI) by the USA in 2000, many countries have accelerated their R&D programs for nanotechnologies. The amount of governmental investment for nanotechnology R&D in 2005, for example, ran over 40 billion US$, which corresponds to a fivefold increase over the investment in 2000 [1]. In accordance, various nanomaterials and structures have been fabricated and utilized with the aim of creating new functions. Nanotechnology is expected to be a powerful driving force for industry in the 21st century. To encourage and promote its development, a trial has begun in which a special mark is placed on products fabricated by nanotechnology [2]. However, a negative social response toward nanotechnology has appeared based on a fear that engineered nanomaterials might be harmful to human health [3]. Thus, the standardization of nanotechnology has become an important and urgent issue in offering a scientifically sound basis for both supporting the positive aspects and examining the negative impact of nanotechnology.

The standardization of nanotechnology was first initiated as actions on national or regional levels in the USA, EU, and Asia. These were followed by the International Organization for Standardization (ISO) Technical Committee (TC) 229 on "Nanotechnology," which started activities in November 2005. This committee currently has 4 working groups (WG), among which WG2 is for “Measurement and Characterization” of nanotechnology. WG2 is also supported as a joint activity (JWG2) by the International Electrotechnical Commission (IEC) TC113 on "Nanotechnology Standardization for Electrical and Electronic Products and Systems."
The activities of ISO TC229 have stimulated discussion on nanotechnology standardization among various organizations concerned with standardization. In Japan, the practical need for nanotechnology standardization was investigated through a questionnaire survey of stakeholders in nanotechnology businesses. Figure 1 shows the results of the survey on key factors and sizes for the realization of new functions by using nanotechnology [4]. It is clear from the results that most of the stakeholders surveyed recognize the importance of shape and size control of nanostructures and materials. The results suggest that atomic force microscopy (AFM) would be a powerful measurement tool for satisfying the need for shape and size measurements.

![Figure 1](image.png)

**Figure 1.** Results of the questionnaire survey on (a) key factor and (b) key size to realize new function by nanotechnology. The analysis bases on the answers from 27 Japanese companies replied to the questionnaire survey. [4].

The standardization of AFM measurements has been discussed by the ISO TC201 (Surface Chemical Analysis) subcommittee (SC) 9 on “Scanning Probe Microscopy.” Precise knowledge of AFM probe shapes as well as proper adjustment (calibration) of AFM equipment are essential for accurate nanostructure measurements, since an AFM image is given as the convolution of the actual surface morphology and the probe shape.

The aim of the present paper is to introduce current standardization activities for nanotechnology, especially the measurement and characterization of nanomaterials and nanostructures. Current working items of ISO TC229/WG2 are described in general together with a description of the working item on AFM probe-shape measurement, which is under discussion by ISO TC201/SC9. The reference material prepared for AFM probe-shape measurement is also explained in detail.

2. Standardization activities for nanomaterial measurement and characterization

2.1. Brief overview of ISO TC229 activities

ISO TC229 on "Nanotechnology" began operation in November 2005 and has convened 7 general meetings. The number of participants has increased each time, with more than 200 people attending the 7th meeting held in Shanghai, China in November 2008. At present, 30 national bodies (i.e., countries) serve as P-members (active contributors with the right to vote) and 10 are O-members. The scope of TC229 clearly states that it focuses on standardization in the field of nanotechnologies, which includes the followings:

1) Understanding and control of matter and processes at the nanoscale, typically, but not exclusively, below 100 nanometers in one or more dimensions where the onset of size-dependent phenomena usually enables novel applications.

2) Utilizing the properties of nanoscale materials that differ from the properties of individual atoms, molecules, and bulk matter, to create improved materials, devices, and systems that exploit these new properties.
The present 4 WGs in ISO TC229 are illustrated in figure 2. The specific tasks of each WG are to develop standards for the followings: unambiguous and uniform terminology and nomenclature (WG1); measurement, characterization, and test methods with consideration of metrology and reference materials (WG2); science-based health, safety, and environmental aspects (WG3); and materials specifications (WG4). Among them, WG1 and WG2 are working jointly with IEC TC113 as mentioned above.

![Figure 2. Structure of ISO TC229 on Nanotechnology.](image)

2.2. Current activities of WG1, WG3, and WG4

As the output of WG1 and WG3 activities, ISO TC229 has published 2 standardization documents (Table 1): a technical report (TR) and a technical specification (TS).

| Document No. | WG | Title of document |
|--------------|----|-------------------|
| ISO/TR 12885:2008 | WG3 | Health and safety practices in occupational settings relevant to nanotechnologies |
| ISO/TS 27687:2008 | WG1 | Terminology and definitions for nano-objects - Nanoparticle, nanofibre and nanoplate |

The purpose of a TR is to circulate data obtained from surveys carried out among the national bodies or "state of the art" data in relation to standards for a particular subject. A TS, in contrast, usually presents prospective standards for provisional application in reply to an urgent request for guidance to meet an identified need. A TS will usually be reviewed 3 years after its publication to consider its conversion into an International Standard (IS) with additional information.

Since standardization should be aligned with the continuing research and development of nanotechnology, ISO TC229 discusses many more TSs and TRs than ISs. The official time period for the publication of a standardization document is 24 months for a TS or TR, and 36 months for an IS. Other main projects discussed in WG1, WG3, and WG4 include the followings: terminology relating to carbon nano-objects, nanostructured materials, bio-nano interfaces, etc. (WG1); methods for endotoxin and inhalation toxicity testing, and guidelines for the safe handling and disposal of manufactured nanomaterials (WG3); specification guidelines for nano-calcium carbonate, nano-titanium oxide, etc. (WG4). Notably, guidance for the physicochemical characterization of engineered nanoscale materials for toxicological assessment is now under discussion jointly between WG3 and WG2 to help the activity of the Organisation for Economic Co-operation and Development (OECD).
2.3. Current activities of WG2

At the 2nd ISO TC229 meeting held in Tokyo during May 2006, WG2 agreed to set as its first target the standardization of carbon nanomaterials. On the basis of this decision, the convener of WG2 circulated a survey containing a list of various measurement properties and possible measurement methods for experts in member bodies to complete. The survey asked whether each measurement property was important and useful for suppliers or for users with appropriate quality control, and if a given method was already well-established for the characterization of multiwall carbon nanotubes (MWCNTs). The properties and measurement methods that received a high grade of importance in the survey are listed in table 2. The protocols for the measurement of CNTs with the methods, together with their principles and descriptions of experimental results, are now under preparation as TS10929 by the project group (PG5) of TC229 WG2.

Table 2. Category, property, and methods for characterizing MWCNT described in the work item of ISO TC229/WG2/PG5 (TS10929).

| category                  | property                        | method                              |
|---------------------------|---------------------------------|-------------------------------------|
| purity                    | moisture content                | weight loss measurement             |
| purity                    | ash content                     | weight loss measurement             |
| purity                    | metallic residual content       | ICP-AES\(^a\), XRF\(^b\)            |
| purity                    | volatile content                | weight loss measurement             |
| purity                    | polyaromatic hydrocarbons       | HPLC-MS\(^c\)                       |
| purity                    | carbon materials excluding MWCNT| SEM                                 |
| purity                    | disorder                        | Raman spectroscopy                   |
| physical property         | burning property                | TG/DTA\(^d\)                        |
| physical property         | stacking nature                 | XRD\(^e\), TEM                       |
| geometrical property      | inner diameter                  | TEM                                 |
| geometrical property      | outer diameter                  | SEM and/or TEM                      |
| geometrical property      | length                          | SEM or TEM                          |
| geometrical property      | morphology                      | SEM and/or TEM                      |

\(^a\)ICP-AES: Inductively Coupled Plasma- Atomic Emission Spectroscopy
\(^b\)XRF: X-ray fluorescence analysis
\(^c\)HPLC-MS: High Performance Liquid Chromatograph- mass spectrometer
\(^d\)TG/DTA: Thermogravimetric/ Differential thermal analysis
\(^e\)XRD: X-ray diffractometer

For the characterization of single-wall carbon nanotubes (SWCNTs), however, the WG2 decided to follow the steps proposed by ANSI (USA), which has proposed the adoption of a layered approach to standardization. The first layer consists of the characterization of purity and structure, which will be followed by the characterization of the electrical, magnetic, mechanical, and optical properties. Moreover, ANSI has proposed to limit the measurement methods for the initial screening step in the first layer. Therefore, the methods chosen for the initial screening step are 1) transmission electron microscopy (TEM), 2) scanning electron microscopy (SEM), 3) ultraviolet (UV)-visible-near-infrared (NIR) absorption, 4) NIR-photoluminescence (NIR-PL) spectroscopy, 5) evolved gas analysis-gas chromatograph mass spectrometry (EGA-GCMS), 6) thermogravimetric analysis (TGA), and 7) Raman spectroscopy. Presently, TSs for the characterization of SWCNTs by these 7 methods are underway in ISO TC229/WG2. Member bodies of ANSI, JISC (Japan), and KATS (Korea) are mainly responsible for the preparation of these documents.
The standardization of CNTs is quite important and urgent since the potential risks of CNTs (e.g., the possibility of inducing mesothelioma) have recently attracted much attention [5, 6]. Experiments for potential risk assessment should use well-established test protocols and well-characterized test samples. Most of the 7 TS documents will be published by the end of 2009, and will provide common protocols for the characterization of test samples. Another discussion item in TC229/WG2 on the “General Framework for Determining Nanoparticle Content in Nanomaterials by Generation of Aerosols,” which is led by DIN (Germany), will also contribute to the establishment of test protocols.

3. Standardization activities regarding nanostructure measurements by AFM

3.1. Current problems with AFM measurements

Although AFM is well known to have very high resolving power for spatial imaging, such as in the observation of an atomic arrangement on a solid surface, the following problems have been indicated. When two protrusive nanostructures with a narrow gap between them are measured, the depth measured between the two structures ($H_m$) is shallower than the height of the protrusion ($H_o$), as is shown schematically in figure 3(a). In addition, in the measurement of an isolated protrusive nanostructure, the measured width ($W_m$) is wider than the width of the original structure ($W_o$), as is shown in figure 3(b). In both cases, the difference between the measured value of the width or height and the real value is related to the shape of the probe used for the AFM observation. The shapes of the probe contour and apex are responsible in the former and latter cases, respectively. Moreover, there is no practical way to know the real probe shape (i.e., probe apex and contour) under in-situ measurement conditions.

![Image of closely placed nanostructures](image1)

![Image of isolated nanostructure](image2)

**Figure 3.** Schematic illustration of AFM measurement results for (a) closely placed two nano-structures and (b) an isolated nano-structure

3.2. AFM probe characterizer for in-situ measurement of a probe shape

To characterize the shape of an AFM probe, especially of the probe contour, it is useful to know the relationship between the probe width ($W$) and the length measured from the probe apex ($L$), as is shown schematically in figure 4(a). This relationship can be easily estimated under in-situ conditions when a probe characterizer with a comb-shaped structure (figure 4(b)) is used. The value of $W$ is obtained from the designed gap width of a rectangular hollow in the probe characterizer, and $L$ can be measured from the trajectory (corrugation) of the AFM probe during measurement of the characterizer. The length at a thicker part of the probe ($L_2$) is obtained from a wider hollow ($W_2$ in figure 4(b)), while that at a thinner part ($L_1$) is obtained from a narrower hollow ($W_1$ in figure 4(b)). Therefore, a probe characterizer with a comb-shaped structure with many different gap widths is necessary to obtain reliable information about the contour of an AFM probe.

As a preliminary step, we fabricated a tip characterizer with a comb-shaped structure having different line and space widths (10, 20, and 60 nm) and a knife-edge structure (figure 5(a)) [7]. For the 20-nm comb-shaped pattern, 10 periodic line/space structures were designed and fabricated.
considering that it will be possible to calibrate the periodicity of the line/space structures by using metrological electron microscopy or metrological AFM [8]. The calibrated structures will add the function of an absolute length scale to the characterizer. An AFM image of the probe characterizer is shown in figure 5(b). The comb-shaped pattern and the knife-edge structure are clearly imaged, although most of the lines appear wider than their actual sizes owing to the size of the AFM probe used for the observation.

3.3. Fabrication of an AFM probe characterizer with a comb-shaped structure

To measure a probe shape precisely, the probe characterizer should have many line and space widths in the range between a few and over a hundred nm. We fabricated another characterizer with 14 line and space structures within the width range from 5 to 100 nm [9]. It is well known that the metal organic chemical vapor deposition (MOCVD) method allows control of film thickness with high
accuracy for a semiconductor compound such as GaAs. Thus we have adopted the MOCVD method for the fabrication of the probe characterizer. Details of the fabrication process are described elsewhere [7]; here we briefly introduce the process for better understanding of the probe characterizer.

GaAs and GaInP layers were alternately grown by the MOCVD method on a GaAs substrate to form multiple sets of GaAs/GaInP layers. The thicknesses of the layers were controlled precisely to realize the desired structure. The thickness accuracy depended on the deposition rate and the intermixing of layers at the interfaces: the error was less than 2 nm in the case of the characterizer shown in figure 5. After the film was grown on a GaAs wafer by the MOCVD method, the wafer was cut into pieces in the vertical direction. The cross-sectional surface of each piece was polished until the surface roughness was less than 1 nm rms (root mean square), and then was etched with a solution containing sulfuric acid and hydrogen peroxide. Since GaAs has an etching rate in this solution about 1000 times higher than GaInP, only the GaAs parts were selectively etched while the GaInP parts retained their original height. Thus the probe characterizer could be fabricated with GaInP layers as lines and GaAs layers as spaces in a comb-shaped structure.

3.4. Standardization and utility of the in-situ probe shape measurement with the characterizer

A new work item with the title "Procedure for in-situ characterization of AFM probes used for nanostructure measurement" has been submitted to ISO TC201/SC9. It is clearly stated in the work item that the standard method is appropriate for characterizing the profile of a probe by determining a probe-shape function, and that it can reduce the uncertainty of AFM measurements of nanostructures.

Nanostructures are now widely used in practical industrial applications. For example, the sensor of a magnetic hard disk is designed to have a sharp concave structure (38 nm in depth and 65 nm in width). However, because it is still premature to use AFM observation for industrial applications and standardization is needed for reliable measurements, cross-sectional TEM observation has been used to evaluate fabricated nanostructures although its cost is higher and the sample preparation time is longer [10].

If we want to measure a fabricated structure by AFM, we have to determine whether the probe to be used for the measurement is sharp enough. A measurement of the probe-shape function based on the proposed standard will make the determination, as shown schematically in figure 7(b). The green area corresponds to the condition that the probe length is larger than 38 nm when its width is narrower than 65 nm. Since the probe-shape function of probe A passes through the green area, but that of probe B does not, only probe A can be used for the AFM measurement.

![Figure 7](image-url). (a) Example of an industrial application of nanostructure. (b) Example for the judgment of AFM probe applicability using a probe-shape function.

Another important issue for the measurement of the probe-shape function by means of the characterizer is that we have to control and adjust the amplitude of the cantilever used for the AFM observation. To optimize the motion of the AFM cantilever, the standard protocol recommends measuring the knife-edge structure together with the comb-shaped structures. The details will be addressed, and the results will be published in the near future. An accurate probe-shape function can
also be used to evaluate the true dimensions of nanomaterials by means of the reproducible restoration technique for distorted AFM images [11].

4. Summary
The current standardization activities on nanotechnology, especially those related to the measurement and characterization of nanomaterials and structures and that have been promoted by ISO TC229/WG2 and ISO TC201/SC9, have been described in detail. The standardization activities not only assist industrial applications of nanomaterials and structures, but also support assessment of their potential risks to human health.

TC229/WG2 started its activity by focusing on carbon nanomaterials, especially CNTs. Other target items of standardization will be the measurement and characterization of fullerene together with those for engineered nanoparticles such as titanium dioxide, zinc oxide, and silicon dioxide. These materials are targeted because they are produced in larger amounts than SWCNTs and MWCNTs, and because they have been selected as target materials by OCED working programs. The standardization of coatings and nanostructured materials (composites and porous structures) will also be discussed together with the basic metrology at the nanoscale as described in the outline strategy for ISO TC229/WG2 [12].

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