

Topics

VAMAS Pre-Standardization Study on Nanoscale Electric Potential Measurement by Kelvin Probe Force Microscopy

Fujita Daisuke^{1*}, Kitahara Masayo², Onishi Keiko²

¹ Corporate Planning Division,

² Research Center for Advanced Measurement and Characterization
National Institute for Materials Science (NIMS)

Scanning probe microscopy (SPM) is a surface chemical analysis technique that can measure the shape, properties, and function of material surfaces at the nanoscale. Kelvin probe force microscopy (KPFM), a type of SPM, is a non-contact type of atomic force microscopy (AFM) that allows visualization of the contact potential difference (CPD) between the tip and sample surface at the nanoscale. 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 a practical protocol for quantitative nanoscale potential measurements on conductive sample surfaces by KPFM. Furthermore, the ISO (International Organization for Standardization) is aiming for international standardization of quantitative nanoscale surface potential measurement by KPFM. Here, we will introduce the recent progress of the pre-standardization project on nanoscale potential measurement using KPFM, which we have been promoting as a project leader in VAMAS.

1. Introduction

VAMAS/TWA 2 (surface chemical analysis) is an international collaborative scheme for the pre-standardization of surface chemical analysis methods in terms of quantification, sensitivity, and resolution. We will work through the round-robin test (RRT) for inter-laboratory comparison (ILC). TWA 2 houses the program areas of mass spectrometry, scanning probe microscopy (SPM), electronic and optical spectroscopy, and data-driven metrology.

Kelvin probe force microscopy (KPFM) is a non-contact variant of atomic force microscopy (AFM). This enables visualization of the contact potential difference (CPD) between the probe tip and the sample surface with nano-resolution.¹⁾ If the potential at the tip of the probe is known, the surface potential of the object can be quantitatively evaluated. Surface potential is related to many surface phenomena and device functions. Therefore, KPFM is applied in various advanced fields such as solar cells, all-solid-state batteries, quantum devices, etc.^{2, 3)} For quantitative surface potential measurements by KPFM, it is important to establish a standard protocol using certified reference materials (CRMs). CRM is used for quantitative potential measurement

and spatial resolution evaluation. The RRT project on KPFM (A12) was proposed by the authors in the SPM area of TWA 2. The objective of this RRT project is to establish a practical protocol for quantitative surface potential measurement by KPFM and eventually to standardize internationally the guidelines for quantitative nanoscale surface potential measurement by KPFM.

This paper introduces the progress of pre-standardization research in VAMAS/TWA2/SPM on quantitative nano-potential measurement by KPFM, for which the authors have been in charge.

2. RRT for quantitative potential measurement by KPFM

For quantitative surface potential measurement by KPFM, it is important to first select an appropriate CRM and then to establish a standard protocol for CPD quantitative measurement. CRMs for quantitative potential measurements are used to determine the work function of the probe tip and to quantitatively measure the CPD values. In this RRT, (1) Au(111) thin films deposited on mica substrates, and (2) highly oriented pyrolytic graphite (HOPG) were proposed as CRM candidates for quantitative surface potential measurement. The reason for selection is that the surface is

*E-mail: FUJITA.daisuke@nims.go.jp

uniform and stable in an atmospheric environment. KPFM probes with Cr / PtIr5 coating were subjected to RRT. The radius of curvature of the tip of the probe is ~25 nm. The purpose of this RRT is to find an appropriate CRM and establish a practical protocol for quantitative potential measurement at sample surfaces by KPFM. Seven institutions from three countries participated in the RRT.

【CPD measurements with bias voltages applied to sample】

The objective is to perform a quantitative evaluation of the CPD values measured by KPFM using a bias voltage applied externally to a conductive sample. Bias voltages were applied to the Au(111) thin film from + 2.0 to - 2.0 V in 1.0 V intervals. If the KPFM measurement system is functioning properly, the interval between measured CPD values should be the change in externally applied bias voltage (1.0 V). If there are unignorable deviations, the accuracy of the sample applied bias voltage or the probe applied bias voltage should be checked. Figure 1 shows examples of CPD images obtained while varying the applied sample bias voltage from + 2.0 V to - 2.0 V.

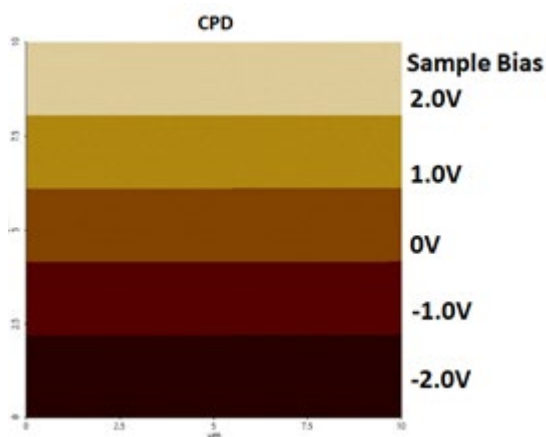


Figure 1: CPD images obtained while varying the sample bias

CPD values reported from RRTs showed CPD changes equal to the applied bias voltage (Figure 2). Data are plotted by the absolute shift from zero bias. The deviation from the expected CPD value averaged in all participant data is 0.05 V and the relative deviation is about 1%. Participants' CPD measurements were found to have a margin of error of less than 1%.

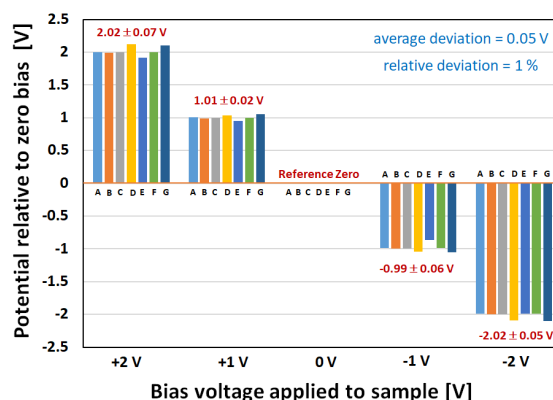


Figure 2: RRT results: CPD values observed from the zero bias positions when sample bias voltages are applied.

【Time stability in CPD measurements for CRM candidates】

The work functions of polycrystalline Au and Au(111) in a vacuum are reported to be 5.1 eV and 5.3 eV, respectively.^{4,5)} Relatively older papers have reported values around 4.8 eV for the work function of Au, but surface contamination may be the cause of the difference.^{6,7)} Polycrystalline Au has been used in some cases to estimate the material surface potentials by KPFM.⁸⁾ On the other hand, the work function of graphite is reported to be 4.6 eV in most cases⁹⁻¹¹⁾ and it has been used as the reference material for surface potential estimation in recent years.^{12,13)} HOPG must be cleaved by the mechanical peeling method just before measurement. The newly cleaved HOPG surface is used as a potential reference sample for KPFM measurements. The purpose of this test is to evaluate the time dependence of stability in the CPD measurements of CRM candidates. Typical topographic and CPD images of five consecutive measurements in the case of Au(111) thin film and HOPG are shown in Figures 3 and 4, respectively. Five CPD histograms were extracted from the corresponding CPD images, by which the time dependence and reproducibility of CPD measurements were evaluated.

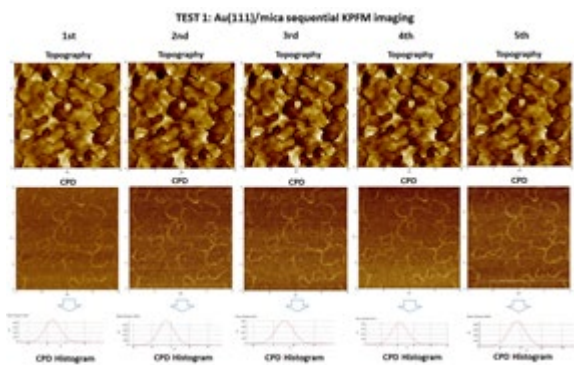


Figure 3: Topographic images, CPD images, and CPD histograms acquired in series on Au(111).

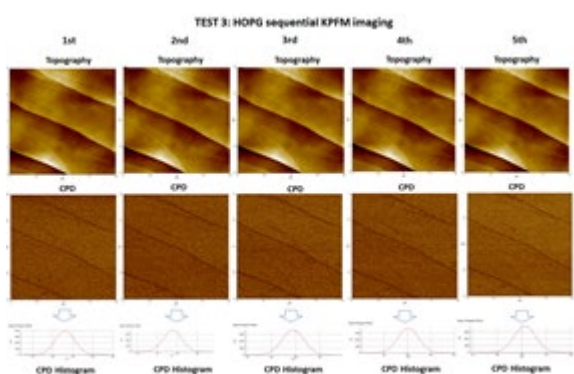


Figure 4: Topographic images, CPD images, and CPD histograms obtained serially on HOPG.

From the RRT results at Au(111), some outliers with a relatively large standard deviation of about 0.1 V were observed, but most of the measured CPD values were accompanied by a much smaller standard deviation of a few mV. This indicates that the time stability of CPD measurement on Au (111) thin film is good. The observed CPD values clearly indicate that the difference in work functions between the PtIr5-coated tip and Au is relatively small, about 0.1 eV. In the case of HOPG, CPD values showed relatively small standard deviations of less than 10 mV. This indicates very good time stability or reproducibility of CPD measurements in HOPG.

【Alternating CPD measurements of Au and HOPG】

The purpose of this RRT is to verify the procedure of work function quantification by alternately measuring CPD between Au (111) thin film and HOPG. Figure 5 shows examples of topographic and CPD images of Au thin films and HOPG measured alternately. RRT results for quantitative work function evaluation are shown in Figure 6. From the average value of $\Delta CPD = CPD(HOPG) - CPD(Au)$, we can say

that the difference in work functions between HOPG and Au thin films is about 0.3 V. Given the work function of V.HOPG as a reference, the work functions of the tip of the probe and the Au thin film can be quantitatively estimated.

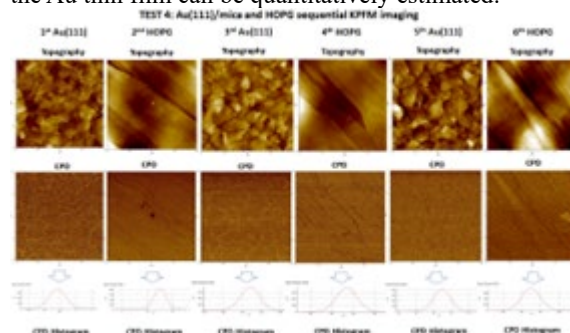


Figure 5: Topographic images, CPD images, and CPD histograms obtained alternately for Au(111) and HOPG.

【Summary】

The following results were obtained through RRTs on quantitative CPD measurements by KPFM. It can be concluded that the Au(111) thin film is quite good in terms of time stability and reproducibility as a CRM for potential measurements, whereas HOPG is very good. In the case of Au thin film, it should be noted that surface contamination may develop after repeated measurements under atmospheric conditions. On the other hand, HOPG was found to have several advantages over Au thin films. First, previous studies have reported that the work function of HOPG is nearly constant (4.6 eV) both in air and vacuum. Second, the use of cleavage by mechanical peeling methods can create a clean single-crystal surface that is free of defects even in atmospheric environments. Based on the above observations, the cleaved HOPG nascent clean surface can be recommended as a CRM as an appropriate potential reference for quantitative potential measurements by KPFM.

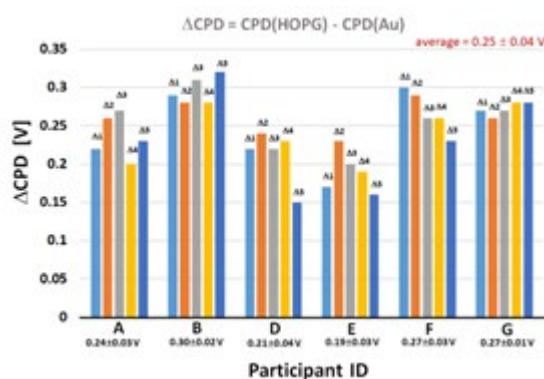


Figure 6. RRT results: alternating CPD measurements of Au thin film and HOPG

3. RRT for quantitative evaluation of spatial resolution

Local surface potentials are related to diverse surface/interface functions. Therefore, KPFM has various application developments in the fields of energy, environment, electronic devices, etc. For nanoscale visualization of surface potential distribution by KPFM, it is important to establish a standard protocol for the quantitative evaluation of spatial resolution in CPD imaging using CRM. The purpose of this RRT is to establish a working protocol for the quantitative evaluation of the spatial resolution of CPD microscopy. The effectiveness of the proposed CRM was evaluated by assessing the spatial resolution obtained in several measurement modes possessed by the participating institutions, demonstrating the suitability of the proposed protocol for the quantitative assessment of spatial resolution. **【CRM for spatial resolution evaluation】**

Single-crystal graphene layers attached by mechanical exfoliation on SiO₂ thin film/Si(100) wafers (90 nm thick) were employed as CRM candidates for quantitative evaluation of spatial resolution. Graphene surfaces have relatively large, atomically flat regions separated by monatomic steps. It was selected as an appropriate CRM because it can discriminate the number of atomic layers with an optical microscope and has different work functions depending on the number of atomic layers. Another advantage is that graphene is stable and chemically inert in atmospheric environments and in a vacuum.

RRT participating institutions obtained data to quantify the spatial resolution of CPD imaging by measuring the boundary region formed by atomic steps between different layer number regions of monolayer and bilayer graphene. First, a relatively large scanning area is used to explore and select areas containing graphene layers of various thicknesses. The selected region must contain at least one monolayer and one bilayer graphene region boundary. Next, topographic and CPD images of a relatively narrow region near the boundary are acquired using a larger-than-normal number of lateral pixels. Typical topographic and CPD images of the atomic step boundaries of mono- and bilayer graphene in AM-KPFM mode are shown in Figure 7.

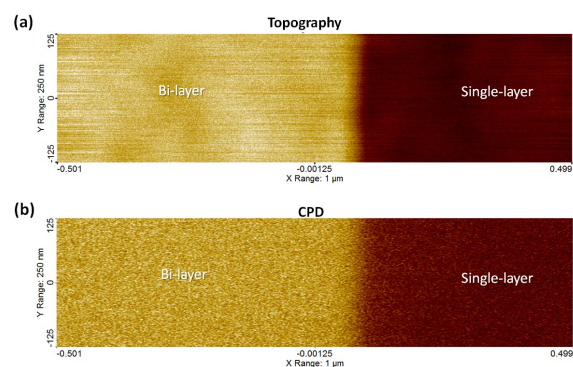


Figure 7: Topographic and CPD images measured at the boundary region between single and bilayer graphene.

【Spatial resolution evaluation of CPD imaging】

The straight-edge method is used to measure spatial resolution at atomic step boundaries between regions with different numbers of graphene layers.¹⁴⁾ The straight-edge method provides a parameter $D_{x-(100-x)}$ that characterizes the steepness of the Edge Spread Function (ESF).¹⁵⁾ The ESF is the convolution of the edge profile and the Line Spread Function (LSF). While the LSF determines the spatial resolution, the graphene boundary width is on the atomic scale and can be regarded as approximately equal to the ESF. Values of 10, 12, 16, or 20 are commonly used for x in $D_{x-(100-x)}$. For example, D_{10-90} is the distance between the 10% and 90% intensity points of the line profile. D_{16-84} provides twice the 2σ (σ : standard deviation) width of the Gaussian resolution function, which was adopted as the spatial resolution in the RRT. The mean and standard deviation of D_{16-84} are extracted from line profiles (10 lines) in the graphene boundary region. A typical example of extracting spatial resolution using a profile across a linear boundary is shown in Figure 8.

Eight institutions from four Asian and European countries participated in the RRT. Ten data sets were collected because two institutions submitted two different types of data using different types of KPFM modes. AM-KPFM was mainly used, but FM-KPFM and PM-KPFM were also used. PM is an abbreviation for phase modulation. PM-KPFM is a similar measurement mode to FM-KPFM in that it uses force gradients to minimize electrostatic interactions.¹⁶⁾

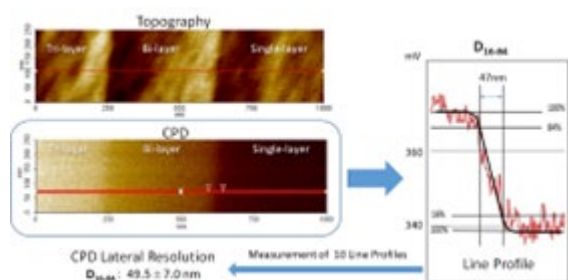


Figure 8. Spatial resolution extracted from line profiles orthogonal to the straight boundary between single and bilayer graphene.

【RRT result analysis】

The means and standard deviations reported from the spatial resolution measurements RRT of the graphene boundaries are summarized in Figure 9. The measurement mode is shown near the marker. It became clear that the data could be clearly divided into two groups. One is a relatively large group with an average spatial resolution of 54 nm and consists only of AM-KPFM modes. The other group is relatively small, with an average spatial resolution of 24 nm, and consists of FM-KPFM and PM-KPFM modes. The observed groupings clearly indicate that FM-KPFM and PM-KPFM have better spatial resolution than AM-KPFM. This observation is valid because FM-KPFM and PM-KPFM detect the gradient of the electrostatic force, whereas AM-KPFM detects the electrostatic force itself. Compared to the typical radius of curvature of the tip of the probe (25 nm), the average spatial resolution of 54 nm in the case of AM-KPFM corresponds approximately to the diameter of the tip apex. In contrast, for FM-KPFM and PM-KPFM, the spatial resolution can be considerably smaller than the diameter of the probe tip.

【Summary】

The following findings were extracted through the RRT on quantitative evaluation of the spatial resolution of CPD imaging by KPFM. Graphene adhered to SiO₂/Si(100) wafers by mechanical exfoliation method was selected as the CRM for spatial resolution measurement of CPD imaging by KPFM due to its very flat and smooth surface and different work function regions for the different number of layers such as single layer and double layer. Graphene with the different number of layers is separated by monatomic step boundaries and is stable in atmospheric environments. Atomic width step boundaries between different graphene layers (single layer and bilayer) were used as straight edges for spatial resolution measurements in RRT. Among some definitions of spatial

resolution, we adopted the transition distance (D_{16-84}) between the intensity points of 16% and 84% of the line profile across the boundaries of the graphene layer. The RRT results following the specified measurement and analysis procedures clearly showed that the graphene layer on SiO₂/Si is a suitable CRM for quantitative evaluation of the spatial resolution of CPD imaging by KPFM.

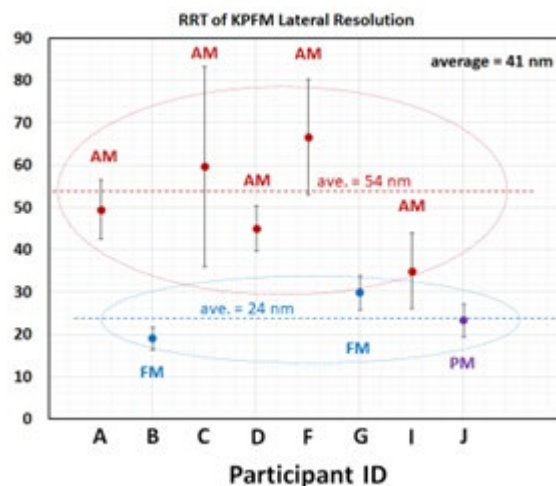


Figure 9. Mean and standard deviation of spatial resolution extracted from line profiles crossing graphene boundaries

6. Summary

Two interlaboratory comparison RRTs were performed in VAMAS /TWA 2 to quantitatively measure surface potentials using KPFM and to quantitatively assess the spatial resolution of CPD imaging. The following key findings related to establishing standard measurement and analysis procedures and CRMs were successfully obtained.

For the RRT on quantitative measurement of surface potential, two candidates were tested as CRMs for CPD measurement by KPFM: Au(111)/mica and HOPG. In the case of Au(111)/mica, it was noted that surface contamination may increase measurement uncertainty when measured for long periods of time in the air. On the other hand, the HOPG was found to have multiple advantages. For example, the work function of HOPG is reported to be nearly constant in both air and vacuum, and mechanical deburring can be used to create fresh, nearly defect-free, clean surfaces in the air. Overall RRT observations conclude that cleaved HOPG

neoplastic surfaces are suitable CRMs for quantitative potential measurements by KPFM. It was found that the use of HOPG as a potential reference allows reproducible evaluation of the work function value at the tip of the probe, leading to quantitative measurement of the surface potential of conductive materials by KPFM.

For the latter RRT, a graphene layer adhered by mechanical exfoliation method on SiO₂/Si(100) wafers was selected as the CRM for spatial resolution evaluation of CPD imaging by KPFM. Its suitability as a CRM for quantitative assessment of spatial resolution in CPD imaging was clearly demonstrated by interlaboratory comparison of spatial resolution data obtained according to the specified measurement protocol and data analysis.

Based on the valuable findings from the international collaborative RRT project in VAMAS/TWA 2, the next step is a new work item proposal (NP) for an international standard to ISO/TC 201/SC 9 (scanning probe microscopy), which is responsible for standardization of scanning probe microscopy.

References

- 1) M. Nonnenmacher, M. P. O'Boyle, H. K. Wickremasinghe, *Appl. Phys. Lett.* **58**, 2921 (1991).
- 2) H. Masuda, N. Ishida, Y. Ogata, D. Ito, D. Fujita, *Nanoscale* **9**, 893 (2017).
- 3) M. Cai, N. Ishida, X. Li, X. Yang, T. Noda, Y. Wu, F. Xie, H. Naito, D. Fujita, L. Han, *Joule* **2**, 296 (2018).
- 4) D. E. Eastman, *Phys. Rev. B* **2**, 1 (1970).
- 5) H. B. Michaelson, *J. Appl. Phys.* **48**, 4729 (1977).
- 6) R. H. Fowler, *Phys. Rev.* **38**, 45 (1931).
- 7) P. A. Anderson, *Phys. Rev.* **115**, 553 (1959).
- 8) M. DeJarld, P. M. Campbell, A. L. Friedman, M. Currie, R. L. Myers-Ward, A. K. Boyd, S. G. Rosenberg, S. P. Pavunny, K. M. Daniels, D. K. Gaskill, *Sci. Rep.* **8**, 16487 (2018).
- 9) K. S. Krishnan, S.C. Jain, *Nature* **169**, 702 (1952).
- 10) T. Takahashi, H. Tokailin, T. Sagawa, *Phys. Rev. B* **32**, 8317 (1985).
- 11) E.V. Rutkov, E.Y. Afanaseva, N.R. Gall, *Diamond & Related Materials*, **101**, 107576 (2020).
- 12) Y.-J. Yu, Y. Zhao, S. Ryu, L. E. Brus, K. S. Kim, P. Kim, *Nano Lett.* **9**, 3430 (2009).
- 13) H. Hibino, H. Kageshima, M. Kotsugi, F. Maeda, F.-Z. Guo, Y. Watanabe, *Phys. Rev. B* **79**, 125437 (2009).
- 14) ISO 18516:2019, Surface chemical analysis –

Determination of lateral resolution and sharpness in beam based methods with a range from nanometres to micrometres (2019).

- 15) W.E.S. Unger, J.M. Stockmann, M. Senoner, T. Weimann, S. Bütetfisch, C. Passiu, N.D. Spencer, A. Rossi, *J. Vac. Sci. Technol. A*, **38**, 053206 (2020).
- 16) E.G. Castanon, A.F. Scarioni, H.W. Schumacher, S. Spencer, R. Perry, J.A. Vicary, C.A. Clifford, H. Corte-León, *J. Phys. Commun.* **4**, 095025 (2020).