
**Surface chemical analysis — Depth
profiling — Non-destructive depth
profiling of nanoscale heavy metal
oxide thin films on Si substrates with
medium energy ion scattering**

*Analyse chimique des surfaces — Profilage d'épaisseur — Profilage
d'épaisseur non destructif de films minces d'oxydes de métaux lourds
à l'échelle nanométrique sur des substrats de Si par diffusion d'ions de
moyenne énergie*

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Foreword

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This document was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 4, *Depth profiling*.

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Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Medium energy ion scattering (MEIS) has been considered to be a quantitative surface and interface composition analysis method with single atomic depth resolution since its invention in the early of 1980s. MEIS has been widely used for ultrathin films, especially nm gate oxides analysis to determine its composition, thickness, and the interface. Recently, MEIS has been used for nanoparticle analysis to determine the size and the composition with the core and shell structure information. In addition to the toroidal electrostatic energy analyser used in the early stage, different types of energy analyser such as magnetic energy analyser and time-of-flight (TOF) energy analyser have been used. With the continued scaling down of electronic devices, demands on accurate and reliable depth profiling have reached beyond the limit of sputter depth profiling which provides deteriorated depth profiles due to the sputter damage. Needs have been risen to investigate the consistency between the three types of energy analyser, ion species, and the different energy range of incident ions used for MEIS analysis and to set up a procedure for quantitative MEIS analysis. Two international interlaboratory tests were performed to develop this document which is reported in [Annex A](#).

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Surface chemical analysis — Depth profiling — Non-destructive depth profiling of nanoscale heavy metal oxide thin films on Si substrates with medium energy ion scattering

1 Scope

This document specifies a method for the quantitative depth profiling of amorphous heavy metal oxide ultrathin films on Si substrates using medium energy ion scattering (MEIS).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 18115, *Surface chemical analysis — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18115 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1

electronic stopping power

retarding force acting on charged particles, typically alpha and proton particles, due to interaction with electrons, resulting in loss of particle energy

4 Principle and recommendations of MEIS analysis

4.1 Ultrathin films of thickness less than 10 nm can be analysed with MEIS. (100 to 500) keV H⁺ or He⁺ ions are used for MEIS analysis. Scattered ion energy and angle are measured precisely so that measured MEIS spectra be compared with simulated MEIS spectra. MEIS spectra can be simulated with various programs from free codes such as PowerMeis¹ and SIMNRA² in public websites, MEIS expert laboratories, and MEIS manufacturers. Simulation programs calculate scattering cross-sections and electronic stopping powers. Quite often, calculated electronic stopping powers are subject to significant errors so that tabulated electronic stopping power values in the IAEA website⁴ are recommended to use.

4.2 If not tabulated, it is recommended to measure electronic stopping power by users for more reliable results. Various types of energy analyzers can be used such as toroidal electrostatic analyser (TEA), magnetic energy analyser (magnetic), and TOF energy analyser. With MEIS analysis procedures specified in this document, less than 10 % uncertainty can be expected for ultrathin films under the guidelines describe in this document. This document is written for amorphous or polycrystalline thin films but not for crystalline thin films. To reduce the uncertainty of MEIS analysis, additional standards

for calibration of scattering geometry, ion energy, energy resolution, detector efficiency, sample alignment, are required.

5 MEIS analysis

5.1 Set the ion scattering conditions such as ion energy, scattering angle, incidence angle from the surface normal, ion species, and ion dose for MEIS analysis. The ion dose is recommended to be in the static condition ($<10^{15}/\text{cm}^2$) but the static requirement for MEIS analysis is not strict compared to surface analysis such as XPS and static SIMS.

5.2 For MEIS analysis, specimen should be flat. Slight contamination due to air oxidation and ambient water and hydrocarbon adsorption does not disturb the MEIS analysis badly. However, if the surface contamination layer is thicker than 1 nm it shall be cleaned by appropriate methods such as solvent washing or ion milling.

5.3 Measure a MEIS spectrum of a specimen and generate a MEIS spectrum file with intensity (counts) vs energy (keV) at a specific angle. Specify all the ion scattering conditions such as ion beam energy, ion species, incidence angle from the surface normal, scattering angle, ion dose or ion current with analysis time, beam radius, and the type of energy analyser.

5.4 For MEIS analysis of ultrathin films of approximately 1 nm thickness, a clear plateau does not appear so that it may have poor reproducibility. It is recommended to express MEIS analysis result in surface areal density rather than in thickness or concentration for MEIS analysis of ultrathin films of approximately 1 nm thickness.

5.5 If the primary ion beam current is too high, it can cause multi-hit problems of detector. Under each MEIS analysis condition, it shall be checked whether the data is affected by the multi-hit problem by comparing MEIS results from high ion beam current and low ion beam current available from each MEIS system.

6 MEIS spectra simulation

6.1 MEIS spectra can be simulated with various programs from free codes such as PowerMeis¹⁾ and SIMNRA²⁾ in public websites and simulation programs from MEIS laboratories and manufacturers as listed in [Annex B](#). Detailed procedures for PowerMeis¹ is also given in [Annex B](#) as an example. In this document, general procedures for MEIS spectra simulation are given as a guidance.

Most of MEIS spectra simulation programs are based on Monte Carlo simulation or analytical calculation of binary scatterings and electronic stopping between binary scatterings. Multiple scattering is suggested to be included in all MEIS simulations. Thin films thicker than 5 nm are strongly recommended to be analysed including multiple scattering for the MEIS data obtained by He ions of ion energy lower than 500 keV. SIMNRA² provides multiple scattering simulation so that users can choose whether including it or not.

Generally, the integration step, and the slab thickness or atom density in MEIS simulations are 0,1 nm, and 0,1 nm or 1×10^{15} atoms/cm², respectively.

In simulation, line shape, cross-section, electronic stopping power, charge neutralization, and energy straggling shall be selected by users as described below. Electronic stopping power is described in detail in [6.2](#)

1) <http://tars.if.ufrgs.br>

2) <https://home.mpcdf.mpg.de/~mam/>

Generally, simple Gaussian can be used as basic line shape for the first approximation. For MEIS systems with high resolution of $\delta E/E$ approximately 8×10^{-4} with proton as a projectile, exponentially modified Gaussian is recommended for ultrathin films. However, other options can be chosen, if needed. Line shape parameters for each element, σ_0 (additional parameter), is calculated by Casp version 5.2³⁾ program for each projectile, projectile energy, and target element. Follow the instructions in Casp version 5.2.

To calculate cross-sections, interatomic potentials can be chosen from Anderson, L'Ecuyer, Moliere potential, or ZBL potential^[1]. For MEIS analysis, Moliere potential is widely used. For energy straggling, Chu or Yang can be usually chosen. For charge neutralization, Marion and Young's equation^[2] is used for 30 keV to 150 keV H⁺ and for 30 keV to 200 keV He⁺ and Armstrong's equation for 400 keV to 500 keV He⁺. Casp charge-state-fractions algorithm³ can be used for He with better reliability and for other heavier ions, if available. PowerMeis provides Marion and Young's equation and Casp neutralization. SIMNRA does not include neutralization in simulation.

6.2 Electronic stopping power is automatically calculated by the SRIM 95 or more recent SRIM2013 code, which can be used for non-critical MEIS analysis with inconsistency higher than 10 %. However, electronic stopping power from the SRIM code can have significant errors in the medium energy range. For accurate MEIS analysis with consistency lower than 10 %, it is recommended to use the measured and tabulated electronic stopping power data of elements and compounds from IAEA⁴⁾, as described in [Formula \(1\)](#). If the IAEA database is insufficient or missing, newly measured electronic stopping power data by appropriate methods can be added to the IAEA database to improve the accuracy of the calculated electronic stopping power. The accuracy of electronic stopping power values in the IAEA database is estimated to be less than 8 % as discussed in [Annex C](#).

The electronic stopping power from IAEA database can be obtained by fitting a set of electronic stopping power data in which can be used in [Formula \(1\)](#). The equation that can be used to fit the IAEA database are given in [Formula \(1\)](#). The E is the ion energy, Z is the atomic number of the ion, m is the mass of the ion. The unit of S_t , S_l , and S_h is eV·cm²/10¹⁵ atoms, that of E is keV, and that of m is u. For fitting to determine A, B, C, and D, Origin or other appropriate fitting programs can be used.

$$\frac{1}{S_t(E)^D} = \frac{1}{S_l(E)^D} + \frac{1}{S_h(E)^D} \quad (1)$$

$$S_l(E) = A\sqrt{E}$$

$$S_h(E) = \frac{z^2 m B}{E} \ln\left(\frac{CE}{m} + 1\right)$$

where

- $S_t(E)$ is the total electronic stopping power;
- $S_l(E)$ is the electronic stopping power of low energy electrons;
- $S_h(E)$ is the electronic stopping power of high energy electrons;
- A, B, C, D are the fitting parameters;
- E is the ion energy;
- z is the atomic number of the ion;
- m is the mass of the ion.

3) Available from: <http://www.casp-program.org/>

4) Available from: <https://www-nds.iaea.org/stopping/>

From the IAEA data⁴, available fitting parameters A, B, C, and D are calculated and tabulated in [Annex D](#) for the convenience of the users of this document.

For straggling correction factor, just use 1,0, if the correction factor is not available, which is generally the case.

6.3 In output, energy channel width and angular channel width can be adjusted according to the energy and angular resolution for each MEIS analysis. Energy channel width is generally used as 0,1 keV and angular channel width should be same to the detector angular width when obtaining 1D spectrum.

In beam, atomic number, atomic mass, beam energy, and incidence angle from the surface normal are given. Projectile number can be adjusted to fit the experimentally measured MEIS spectrum of well-defined internal reference.

Analyser type is chosen among electrostatic, TOF, and magnetic. For electrostatic and magnetic analyser type, energy resolution full width half maximum (FWHM) (δE), scattering angle, and angular width ($\Delta\theta$) specified from each MEIS measurements are given. For TOF analyser type, TOF length (L), time resolution (δt), are additionally given according to specific TOF MEIS scattering conditions. Out of plane angle and angular width are used when MEIS scattering data are obtained from out of plane region or large detector. Energy resolution FWHM (δE) or time resolution (δt) can be measured by fitting the leading edge of a MEIS peak from a clean surface peak of heavy metal specimen.

6.4 After all the input parameters for simulation and experimental parameters are given, the structure of a specimen is to be built. Firstly, list up elements used in simulation. Then, construct layered thin film structures with the thickness and composition for each layer. Generally, a substrate layer is included in simulations. If necessary, a surface contamination layer or an interface layer between ultrathin film layers can be introduced to improve the fitting.

6.5 After all the specified and appropriate values are given, start a simulation. If all the input parameters are appropriate, then simulated spectra are given. Adjust the parameter of the projectile number in beam to fit the overall intensity or the intensity of a reference layer for example between measured and simulated MEIS spectra when an internal reference layer is used. Then adjust the thickness and composition of each layer manually and iteratively to get the best agreement between measured and simulated MEIS spectra. A chi-square test can be used to find the best agreement with a properly chosen energy range of spectrum. The low limit of an energy range in χ^2 calculation is recommended to be not lower than 10 keV from the substrate surface peak. In case that a reference layer of known stoichiometry is included in the sample, the height of reference layer can be chosen to generate minimum χ^2 calculation to determine the projectile number and then the composition and the thickness of unknown layers can be determined by changing fitting energy range to the unknown layer peak position to calculate and minimize χ^2 . In case of no reference layer, overall χ^2 calculation with an appropriate fitting range can be used to get the best agreement between measured and simulated MEIS spectra.

6.6 MEIS simulation programs generate composition and surface areal density (10^{15} atoms/cm²) for each layer. Therefore, to convert the areal density to the thickness of each layer, the density of each layer is required. If the density of thin films used in the MEIS analysis is known, use the number. But, generally the number is not known so that the bulk density can be used. In the case of non-stoichiometric compounds or mixtures, the sum rule can be used. According to the sum rule, the density of a non-stoichiometric compound $\rho(A_{x+\delta x} B_{y+\delta y})$ can be estimated by the [Formula \(2\)](#).

$$\rho(A_{x+\delta x} B_{y+\delta y}) = [(x+\delta x)m(A) + (y+\delta y)m(B)] / \{[x m(A) + y m(B)] / \rho(A_x B_y)\} \quad (2)$$

where

$\rho(A_{x+\delta x} B_{y+\delta y})$ is the density of a non-stoichiometric compound with A constituent of $x+\delta x$ composition and B constituent of $y+\delta y$ composition;

$m(A)$	is the mass of A constituent;
$m(B)$	is the mass of B constituent;
$\rho(A_xB_y)$	is the density of a stoichiometric compound with A constituent of x composition and B constituent of y composition.

For mixtures of A and B, the density of the mixture A(x%) and B(y%) can be estimated by the [Formula \(3\)](#).

$$\rho(x\%A+y\%B) = [x m(A) + y m(B)]/[x m(A)/\rho(A) + y m(B)/\rho(B)] \quad (3)$$

In [Formulae \(2\)](#) and [\(3\)](#), the m is the mass of each element or a compound in u.

By dividing the simulated areal atomic density of each layer with the estimated density of each layer, the thickness of each layer can be obtained. The use of bulk density values or the density estimated by the sum rule can generate errors in the depth from MEIS analysis.

7 Reporting MEIS analysis results

7.1 Report all the MEIS analysis conditions such as ion beam energy, ion species, ion current, incidence angle from the surface normal, scattering angle, ion dose, analysis time, beam radius, sample descriptions including surface contamination and surface flatness, sample preparation, MEIS analysis chamber pressure, energy analyser type and specifications, detector type and specifications.

7.2 Details of MEIS spectra simulations shall be specified including simulation program name and all of simulation parameters.

7.3 It is recommended to report MEIS analysis results in the quantity with unit of surface areal density (10^{15} atoms/cm²), or concentration (atomic fraction) as a function of depth in the unit of areal density (10^{15} atoms/cm²). Using the bulk density, it can be reported as concentration (atomic fraction) as a function of depth in the unit of thickness (nm), but it shall be clearly stated that the bulk densities are assumed for ultrathin films.

Annex A (informative)

Interlaboratory test report

A.1 Overview

This annex gives a report of an interlaboratory test on non-destructive depth profiling of nanoscale thin films with medium energy ion scattering.

A.2 Principle

MEIS spectra of HfO₂ thin films with nominal thickness of 1 nm, 3 nm, 5 nm, and 7 nm on a substrate 12 nm SiO₂ on a Si substrate were measured precisely by 12 participants. Three different types of MEIS detector were used such as electrostatic, magnetic, and TOF. Measured MEIS spectra were simulated by each participant laboratories, resulting in the poor consistency of approximately 15 %. They were simulated again by one key laboratory, K-MAC, Korea and sources of poor consistency such as electronic stopping power and neutralization correction were investigated, which improved the consistency of MEIS analysis results less than 8 %.

A.3 Sample description

Samples were prepared at National Nano Fab Center in Daejeon, Korea. Nominally, 1, 3, 5, and 7 nm HfO₂ were deposited by atomic layer deposition method on a 12 nm thermal SiO₂ layer on a 6 inch Si(001) wafer. A 12 nm thermal SiO₂ layer that assists the uniform and flat growth of HfO₂ layer is used as an internal reference in the MEIS analysis. The uniformity of the thickness over a 6 inch wafer was tested by measuring 7 points of the wafer 5 times with ellipsometer. As a result, the standard deviations of thickness were estimated to approximately 0,5 %. The thickness of HfO₂/SiO₂/Si samples was also measured by transmission electron microscopy (TEM). TEM images of HfO₂/SiO₂/Si thin films are shown in [Figure A.1](#) and the average thickness of samples are summarized in [Table A.1](#).