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Surface chemical analysis — Determination of surface elemental contamination on silicon wafers by total-reflection X-ray fluorescence (TXRF) spectroscopy

Analyse chimique des surfaces — Détermination de la contamination en éléments à la surface des tranches de silicium par spectroscopie de fluorescence X à réflexion totale

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights (see annex D, note to clause D.2). ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 14706 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*.

Annexes A to F of this International Standard are for information only.

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Introduction

This International Standard was prepared for the measurement of surface elemental contamination on silicon wafers on the basis of three existing standards: ASTM F 1526, SEMI Standard M33 and a UCS (Ultra-Clean Society) standard published by the Institute of Basic Semiconductor Technology Development.

TXRF needs reference materials to perform quantitative analyses. Certified reference materials are not available at low densities of 10^{10} atoms/cm^2. Even if they were available, the possibility of contamination from the environment reduces the shelf life of such reference materials.

Therefore, the TXRF reference materials should be prepared and analysed for calibration by each relevant analytical laboratory. Thus, two standards, one for the TXRF measurement procedure and the other for the preparation of reference materials, are necessary. This standard concerns the former part.

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Surface chemical analysis — Determination of surface elemental contamination on silicon wafers by total-reflection X-ray fluorescence (TXRF) spectroscopy

1 Scope

This International Standard specifies a TXRF method for the measurement of the atomic surface density of elemental contamination on chemomechanically polished or epitaxial silicon wafer surfaces.

The method is applicable to:

— elements of atomic number from 16 (S) to 92 (U);

— contamination elements with atomic surface densities from 1×10^{10} atoms/cm^2 to 1×10^{14} atoms/cm^2;

— contamination elements with atomic surface densities from 5×10^{8} atoms/cm^2 to 5×10^{12} atoms/cm^2 using a VPD (vapour-phase decomposition) specimen preparation method (see 3.4).

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 14644-1, *Cleanrooms and associated controlled environments — Part 1: Classification of air cleanliness.*

3 Terms and definitions

For the purposes of this International Standard, the following terms and definitions apply.

3.1
total reflection
complete reflection of incident radiation at a boundary with a medium in which it travels faster

NOTE The refractive index of incident X-rays impinging on silicon is less than 1. X-rays which are incident on the surface at a small glancing angle are therefore totally reflected from the surface at an angle equal to the glancing angle.

3.2
glancing angle
angle between the specimen surface and the X-rays which impinge on the surface

3.3
critical angle
glancing angle corresponding to the first point of inflection in the plot of the sample matrix X-ray fluorescence against the glancing angle

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3.4
VPD-TXRF method
method in which impurities on the surface are collected by the so-called VPD procedure, i.e. the non-volatile products formed by acid decomposition of the oxide at the wafer surface are collected by a droplet of collecting agent, usually ultra-pure hydrofluoric acid, and dried in a manner which gives the least environmental contamination, the residue from the droplet subsequently being analysed by TXRF

3.5
spurious peaks
detected peaks that do not originate from impurities on the silicon wafer

NOTE Spurious peaks are due to X-rays originating from elements in the detector or the X-ray path. The X-rays are excited by direct scattering or reflection of incident X-rays. This phenomenon leads to an increase in the measurement error. Spurious peaks seriously affect analytical measurements in the contamination range from ca. 10^{10} atoms/cm^2 to ca. 10^{11} atoms/cm^2.

4 Abbreviated terms

FWHM full width at half maximum

RM reference material

SSD solid-state detector

TXRF total-reflection X-ray fluorescence

VPD vapour-phase decomposition

5 Principle

When a specimen is irradiated with X-rays, fluorescence X-rays at characteristic energies of the elements that constitute the specimen are generated. The intensities of the fluorescence X-rays are proportional to the amounts of each element in the specimen.

Total reflection of the incident X-rays on the specimen reduces the intensity of the scattered X-rays. This allows more intense excitation of the fluorescence X-rays from the surface region, including atoms deposited on the surface of the silicon wafer. Consequently, a spectrum of fluorescence X-rays with a large ratio of signal to background (S/B) and signal to noise (S/N) can be obtained.

The detection limit depends upon the atomic number, the excitation energy, the photon flux, the detector resolution, the energy bandwidth of the excitation X-rays, the instrumental background, the integration time and the blank value. For constant instrumental parameters, the interference-free detection limits vary over two orders of magnitude as a function of the atomic number of the analyte element.

NOTE The depth of measurement may vary with the glancing angle, but in the case of film-type contamination it is usually less than 5 nm. The area of measurement is ca. 10 mm in diameter, though it varies depending on the relative position of the X-ray detector and the specimen. In the case of particulate-type contamination on a clean surface, the yield of fluorescence X-rays varies depending on the sizes, distribution and constituent elements of the particles.

6 Apparatus

6.1 The apparatus for TXRF shall include at least the following components: an X-ray source, a monochromator, a specimen stage capable of movement in three orthogonal directions, an X-ray detector (SSD) and a computerized signal-processing system.

6.2 X-rays which have been monochromatized shall be used as the incident X-rays.

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6.3 The fluorescence X-ray detector shall have sufficient energy resolution to analyse the Mn-K-$L_{II,III}$ line with an FWHM of 200 eV or less.

6.4 The specimen stage, which sets the glancing angle, shall be controlled to a reproducibility within ± 0,17 mrad (0,01°) in the range between 0 mrad (0°) and 8,7 mrad (0,5°).

6.5 The atmosphere in the specimen chamber shall be able to be brought to a reduced pressure or replaced with helium gas or nitrogen gas, as required.

7 Environment for specimen preparation and measurement

7.1 The local environment (i.e. airborne particles, temperature, humidity) for specimen preparation and measurement shall be equal to or better than ISO Class 4 (see ISO 14644-1).

NOTE The unwanted deposition of airborne particles which are composed of the elements that are being measured will cause an increase in the error of measurement.

7.2 The mechanical vibration at the location where the apparatus is installed shall be as small as possible and shall not be greater than 5×10^{-3} m/s^2 (0,5 Gal).

NOTE The mechanical vibration will degrade the energy resolution of the detection system, which will, in turn, degrade the detection limits and peak deconvolution.

8 Calibration reference materials

8.1 Calibration reference materials (RMs) used to establish a reliable calibration procedure shall consist of an RM on which known amounts of impurities have been deposited and a blank RM used to determine the level of contamination of the RM (see annex A).

8.2 The RMs shall be prepared from a chemomechanically polished wafer with a certain quantity of Ni or Fe uniformly deposited on its surface as the RM element. The atomic surface density of the RM element shall be ca. 1×10^{12} atoms/cm^2 (see annex C).

8.3 How the RM element is located on the RM surface shall be verified by an anglescan (see annex E).

8.4 The amount of RM element deposited on the surface of the wafer shall be determined by a reliable quantitative method of analysis.

8.5 The blank RM shall be a chemomechanically polished or epitaxial wafer. The impurity of the surface region of the blank RM shall be below the detection limit. The crystallographic orientation of the blank RM shall be the same as that of the RM.

8.6 The RM and the blank RM shall be stored in the same container.

9 Safety

This test method uses X-ray radiation. Consequently, it is absolutely essential to avoid exposing any part of the body to the X-rays produced by the apparatus. It is especially important to keep hands and fingers out of the path of the X-rays and to protect the eyes from scattered secondary X-ray radiation. Each country has its own safety regulations and requirements concerning X-rays. These shall be observed.

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10 Measurement procedure

10.1 Preparation for measurement

10.1.1 All specimens shall be chemomechanically polished or epitaxial wafers.

10.1.2 For the VPD-TXRF method, the impurities on the surface are collected by VPD, i.e. acid decomposition in a droplet which is then dried in a manner that produces the least environmental contamination (see annex D).

10.1.3 For a series of measurements, including the calibration measurements, the crystal orientation of the specimen on the specimen stage shall be the same for each specimen.

10.1.4 Set the glancing angle at between 25 % and 75 % of the critical angle.

NOTE Due to the physical form of particulate-type contamination, an angle that is too low will cause a larger error.

NOTE The critical angle is a function of the incident X-ray energy. It is 3,20 mrad (0,18°) for 9,67 keV (W-L_{II}-M_{IV}), 1,78 mrad (0,10°) for 17,44 keV (Mo-K-$L_{II,III}$) and 2,72 mrad (0,16°) for 11,4 keV (Au-L_{II}-M_{IV}).

10.1.5 Set the following parameters as specified:

a) For a rotating anode, the excitation voltage of the X-ray source shall be 30 kV or more, with the excitation current set to 200 mA or more and the integration time set to 500 s or more.

b) For a sealed Mo or W anode X-ray tube, the excitation voltage of the X-ray source shall be 30 kV or more, with the excitation current set to 40 mA or more and the integration time set to 500 s or more.

c) If the X-ray intensity at the detector is too high for the detection system, the excitation current shall be adjusted to a lower value to give an appropriate count rate.

10.1.6 Move the centre of the specimen under the centre of the detector. While rotating the specimen, generate and measure fluorescence X-rays to find the azimuth with the least spurious peaks. When possible, the measurement hereafter shall be conducted at the same azimuth.

If the apparatus does not allow the best-fit azimuth to be set at off-centre positions so as to avoid spurious peaks, care shall be taken when evaluating the surface-mapping data.

10.2 Preparing a calibration curve

10.2.1 Measure the blank RM and determine the integrated intensity of the fluorescence X-rays generated by the blank RM.

10.2.2 Measure the RM under the same conditions as specified in 10.2.1. In the case of the VPD-TXRF method, place the residue from the RM under the centre of the detector.

10.2.3 Verify that the measured value of the integrated intensity of the X-rays generated by the blank RM is less than 10 % of the integrated intensity from the RM.

If the integrated intensity from the blank RM is 10 % or more of that from the RM, discard both the RM and the blank RM and prepare a new set comprising an RM and blank RM.

Carry out this check at appropriate intervals.

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10.2.4 Determine the integrated intensity of the X-rays generated by the RM element by means of procedure a) or b) specified below:

a) Smooth the measured numerical values by digital processing.

Determine the integrated intensity of the X-rays by subtracting the background from the measured numerical values.

b) Determine the Gaussian function that best fits the measured numerical values. Then determine the integrated intensity from the peak height and the half-width of the Gaussian function.

10.2.5 Obtain a calibration curve (a plot of the atomic surface density versus the integrated X-ray intensity from the RM element). The curve shall pass through the origin.

10.3 Measurement of a test specimen

10.3.1 Measure the test specimen under the same conditions as specified in 10.1. If using the VPD-TXRF method, place the residue from the test specimen under the centre of the detector.

10.3.2 Determine the integrated intensity of the X-rays generated by contamination elements in the same manner as specified in 10.2.

When two or more fluorescence X-ray lines overlap, use the method of deconvolution to obtain the integrated intensity of the X-rays for the subject element.

NOTE 1 The repeatability and reproducibility of the measurement for the subject element will vary with the kind of X-ray used.

NOTE 2 Deviation of the glancing angle of the incident X-rays from the set value will increase the measurement error.

NOTE 3 Greater surface roughness will increase the measurement error.

NOTE 4 The values obtained from VPD residues will depend greatly on the physical form of the residue and the elements contained in the residue.

11 Expression of results

11.1 Method of calculation

By using equations (1) and (2), calculate the atomic surface density C_{m} for each of the contamination elements from the results obtained in clause 10.

$$K = \frac{C_{\mathrm{S}}}{I_{\mathrm{S}}} \tag{1}$$

$$C_{\mathrm{m}} = K \times \frac{I_{\mathrm{m}}}{S_{\mathrm{R}}} \tag{2}$$

where

K is the slope of the calibration curve obtained in 10.2.5;

C_{S} is the atomic surface density of the RM element, in atoms/cm^2;

I_{S} is the integrated intensity of the fluorescence X-rays from the RM element, in counts per second (cps);

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C_m is the atomic surface density of the contamination element on the test specimen, in atoms/cm^2;

I_m is the integrated intensity of the fluorescence X-rays from the contamination element on the test specimen, in cps;

S_R is the relative sensitivity factor, which corrects for the difference in sensitivity for each element.

NOTE In order to determine values of the relative sensitivity factor S_R for other elements, measurements are often made on two or more specimens with differing contents of these elements. The results can then be used to prepare calibration curves other than those obtained using theoretical relative sensitivity factors. The relative sensitivity factor can be determined in terms of these curves using the RM element or can be calculated as shown in annex B.

11.2 Blank correction

For measurements below 10^{11} atoms/cm^2, where the instrumental blank is not negligible, the atomic surface density C_m shall be corrected by subtracting the atomic surface density C_0 of a fresh contamination-free specimen, with the same crystal orientation, measured under the same conditions as specified in 10.1 and 10.2 and calculated as described in 11.1.

12 Precision

An international inter-laboratory test programme based on the method specified in this International Standard was carried out by 15 laboratories from Japan, Europe and USA. Four test specimens and one RM were distributed as one set. 17 sets of measurements were obtained from the 15 laboratories. Repeatability and reproducibility were calculated in accordance with the principles of ISO 5725-2 [1]. A statistical report of the inter-laboratory test is given in annex F.

13 Test report

The test report shall include the following items:

a) specimen identification;

b) the kind(s) of X-ray source used, e.g. rotating-anode W-tube;

c) the excitation X-rays used, e.g. W-L_{II}-M_{IV};

d) the voltage applied to the X-ray source, e.g. 30 kV;

e) the current applied to the X-ray source, e.g. 200 mA;

f) the glancing angle used, e.g. 1,8 mrad (0,10°);

g) the integration time, e.g. 500 s;

h) the method used to prepare the RM, e.g. SC1 dip method (see annex A);

i) the atomic surface density of the RM element (Ni or Fe), e.g. Ni $1{,}05 \times 10^{12}$ atoms/cm^2;

j) the measurement location on the test specimen, e.g. centre of wafer;

k) the calibration method used, i.e. procedure a) or b) in 10.2.4;

l) the name(s) of the element(s) on the test specimen and the atomic surface density of each.

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Annex A
(informative)

Reference materials

A.1 Reference materials for this International Standard can be prepared by the SC1 dip method [which uses standard cleaning solution 1 (a silicon wafer cleaning solution consisting of water, ammonia and hydrogen peroxide)] or by the spin-coating method to give a surface Ni or Fe content of ca. 10^{12} atoms/cm^2 (see annex C).

A.2 The Fe RM prepared by the SC1 dip method is preferred when the apparatus is installed in a higher-class cleanroom.

A.3 The Ni RM is more commonly used for routine measurements.

A.4 One or more RMs should be prepared from each lot or batch.

A.5 Specimens from the same lot or batch are assumed to have the same atomic surface density.

A.6 The calibration of RMs is discussed in annex C.

A.7 In the case of VPD-TXRF measurement, an RM consisting of a microdroplet residue containing known amounts of impurities and deposited on a hydrophobic polished or epitaxial wafer can be used.

A.8 The VPD collection efficiency is assumed to be approximately 100 %.

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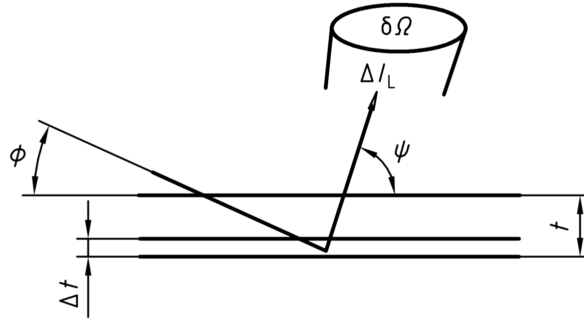
Annex B
(informative)

Relative sensitivity factor

B.1 The relative sensitivity factor can be calculated from the model shown in Figure B.1.



Key

t measurement depth

Ω solid angle

Figure B.1 — Schematic illustration of TXRF

The X-ray intensity ΔI_L of measured spectrum L of element A, generated from the very thin layer Δt is given by:

$$\Delta I_L = I_{0,\lambda_P} \exp\left\{-\left[(\mu/\rho)_{M,\lambda_P}\ \rho t \operatorname{cosec}\phi\right]\right\}(\mu/\rho)_{M,\lambda_P}\ \rho \Delta t \operatorname{cosec}\phi \frac{w_A\ (\mu/\rho)_{A,\lambda_P}}{(\mu/\rho)_{M,\lambda_P}} \times \times \frac{\gamma_A - 1}{\gamma_A}\ \omega_A g_L\ \frac{\delta\Omega}{4\pi} \exp\left\{-\left[(\mu/\rho)_{M,\lambda_L}\ \rho t \operatorname{cosec}\psi\right]\right\} \quad (B.1)$$

where

I_{0,λ_P}	is the incident X-ray intensity at wavelength λ_P;
$(\mu/\rho)_{M,\lambda_P}$	is the mass absorption coefficient for the X-rays incident on specimen M [2];
ρ	is the density of specimen M;
w_A	is the mass fraction of element A in the specimen;
$(\mu/\rho)_{A,\lambda_P}$	is the mass absorption coefficient for the X-rays incident on element A;
γ_A	is the jump ratio of the series shell of element A at the absorption edge [2];
ω_A	is the fluorescence yield of the series shell of element A [2 to 4];
g_L	is the relative transition probability of the measured spectrum L [5];
$(\mu/\rho)_{M,\lambda_L}$	is the mass absorption coefficient of measured spectrum L at wavelength λ_L for specimen M.

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Assuming that the value of the depth t is very small:

$$\exp\left\{-\left[(\mu/\rho)_{\mathrm{M},\lambda_\mathrm{P}}\ \rho t \operatorname{cosec}\phi\right]\right\} = 1$$

$$\exp\left\{-\left[(\mu/\rho)_{\mathrm{M},\lambda_\mathrm{L}}\ \rho t \operatorname{cosec}\psi\right]\right\} = 1$$

Adding double excitation of total reflection, equation (B.1) can be expressed as follows:

$$I_\mathrm{L} = 2 I_{0,\lambda_\mathrm{P}} w_\mathrm{A} (\mu/\rho)_{\mathrm{A},\lambda_\mathrm{P}} \frac{\gamma_\mathrm{A} - 1}{\gamma_\mathrm{A}} \omega_\mathrm{A} g_\mathrm{L} \frac{\delta\Omega}{4\pi} \rho t \operatorname{cosec}\varphi \tag{B.2}$$

As the value of the depth t is very small:

$$w_\mathrm{A} \rho t = C_\mathrm{A} \left(A_{\mathrm{r,A}}/\mathrm{N_A}\right) \tag{B.3}$$

where

C_A is the atomic surface density of element A;

$A_{\mathrm{r,A}}$ is the atomic mass of element A;

$\mathrm{N_A}$ is Avogadro's number.

From equations (B.2) and (B.3):

$$S_\mathrm{A} = \frac{I_\mathrm{L}}{C_\mathrm{A}} = 2 I_{0,\lambda_\mathrm{P}} \frac{\delta\Omega}{4\pi} \left(A_{\mathrm{r,A}}/\mathrm{N_A}\right) \operatorname{cosec}\phi (\mu/\rho)_{\mathrm{A},\lambda_\mathrm{P}} \frac{\gamma_\mathrm{A} - 1}{\gamma_\mathrm{A}} \omega_\mathrm{A} g_\mathrm{L}$$

The relative sensitivity factor S_R is thus given by:

$$S_\mathrm{R} = \frac{S_\mathrm{A}}{S_\mathrm{RM}} = \frac{(\mu/\rho)_{\mathrm{A},\lambda_\mathrm{P}} \frac{\gamma_\mathrm{A} - 1}{\gamma_\mathrm{A}} \omega_\mathrm{A}\ g_\mathrm{L} \cdot A_{\mathrm{r,A}} \cdot E_\mathrm{A}}{(\mu/\rho)_{\mathrm{RM},\lambda_\mathrm{P}} \frac{\gamma_\mathrm{RM} - 1}{\gamma_\mathrm{RM}} \omega_\mathrm{RM}\ g_{\lambda_\mathrm{RM}} \cdot A_{\mathrm{r,RM}} \cdot E_\mathrm{RM}} \tag{B.4}$$

where

$A_{\mathrm{r,RM}}$ is the relative atomic mass of the RM element;

E_A, E_RM are the attenuation factors in the solid-state detector for wavelengths λ_L and λ_RM, respectively.

The above equation is based on the assumption that the specimen has a uniform density and a smooth surface, that monochromatized X-rays with no divergency are used, and that no multiple scattering or excitation by other elements present occurs.

B.2 When these parameters are unknown or only approximate values are required, Table B.1 or Table B.2 is used, provided that the RM element is Ni.

B.3 Table B.1 lists calculated values of S_R, using W-$\mathrm{L_{II}}$-$\mathrm{M_{IV}}$ as the incident X-rays and a solid-state detector with a 12,5-µm-thick Be window. Table B.2 lists the calculated values of S_R using Mo-K-$\mathrm{L_{II,III}}$ as the incident X-rays and a solid-state detector with a 12,5-µm-thick Be window. Under different conditions (e.g. Au anode or carbon filter), the values will have to be calibrated from equation (B.4).

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Table B.1 — Relative sensitivity factors of elements for W-L_{II}-M_{IV}

Atomic No.	16	17	18	19	20	21	22
Spectrum	S-K-$L_{II,III}$	Cl-K-$L_{II,III}$	Ar-K-$L_{II,III}$	K-K-$L_{II,III}$	Ca-K-$L_{II,III}$	Sc-K-$L_{II,III}$	Ti-K-$L_{II,III}$
S_R	0,022 5	0,036 9	0,056 3	0,082 6	0,117	0,168	0,225
Atomic No.	23	24	25	26	27	28	29
Spectrum	V-K-$L_{II,III}$	Cr-K-$L_{II,III}$	Mn-K-$L_{II,III}$	Fe-K-$L_{II,III}$	Co-K-$L_{II,III}$	Ni-K-$L_{II,III}$	Cu-K-$L_{II,III}$
S_R	0,302	0,402	0,517	0,659	0,850	1,000	1,237
Atomic No.	30	33	42	46	47	50	
Spectrum	Zn-K-$L_{II,III}$	As-L_{III}-$M_{IV,V}$	Mo-L_{III}-$M_{IV,V}$	Pd-L_{III}-$M_{IV,V}$	Ag-L_{III}-$M_{IV,V}$	Sn-L_{III}-$M_{IV,V}$	
S_R	1,512	0,004 50	0,044 0	0,081 9	0,093 0	0,146	

Table B.2 — List of relative sensitivity factor of elements for Mo-K-$L_{II,III}$

Atomic No.	16	17	18	19	20	21	22
Spectrum	S-K-$L_{II,III}$	Cl-K-$L_{II,III}$	Ar-K-$L_{II,III}$	K-K-$L_{II,III}$	Ca-K-$L_{II,III}$	Sc-K-$L_{II,III}$	Ti-K-$L_{II,III}$
S_R	0,019 4	0,032 1	0,048 8	0,073 1	0,105	0,153	0,207
Atomic No.	23	24	25	26	27	28	29
Spectrum	V-K-$L_{II,III}$	Cr-K-$L_{II,III}$	Mn-K-$L_{II,III}$	Fe-K-$L_{II,III}$	Co-K-$L_{II,III}$	Ni-K-$L_{II,III}$	Cu-K-$L_{II,III}$
S_R	0,276	0,373	0,483	0,641	0,813	1,000	1,242
Atomic No.	30	33	42	46	47	50	73
Spectrum	Zn-K-$L_{II,III}$	As-K-$L_{II,III}$	Mo-L_{III}-$M_{IV,V}$	Pd-L_{III}-$M_{IV,V}$	Ag-L_{III}-$M_{IV,V}$	Sn-L_{III}-$M_{IV,V}$	Ta-L_{III}-$M_{IV,V}$
S_R	1,538	2,445	0,041 2	0,077 7	0,089 4	0,142	2,253
Atomic No.	74	78	79	80	82	92	
Spectrum	W-L_{III}-$M_{IV,V}$	Pt-L_{III}-$M_{IV,V}$	Au-L_{III}-$M_{IV,V}$	Hg-L_{III}-$M_{IV,V}$	Pb-L_{III}-$M_{IV,V}$	U-L_{III}-$M_{IV,V}$	
S_R	2,566	3,643	3,734	4,015	5,023	5,574	

B.4 Correction factors may be made to allow for the instrumental conditions.

B.5 Instead of using relative sensitivity factors, a calibration curve may be prepared using calibration specimens.

B.6 If such a calibration curve is used, recalibration with RMs will be necessary at appropriate intervals.

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Annex C
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Preparation of reference materials [6]

C.1 Requirements on RMs for TXRF

TXRF is a highly sensitive method of analysis, and the analyte content of RMs is very low compared with that for other analytical methods. Even a little contamination will make an RM unsuitable. Thus, RMs are not suitable for permanent use. Fresh RMs have to be prepared and calibrated from time to time. It is therefore preferable to use an RM which can be prepared and calibrated as easily as possible.

The area of incidence and the flux density of the excitation X-rays vary widely with the glancing angle, and the intensity of the detector signal depends on the relative disposition of the specimen and the X-ray detector [7]. When an RM is calibrated, there is no easy quantitative analytical method that can determine the analyte content exclusively in the small area on the specimen where the TXRF analysis takes place. Therefore, for the preparation of a reliable working RM, it is desirable to use a method which deposits the reference element uniformly over the whole surface of the wafer.

In addition, long-term quality stability is required.

Specific methods of preparing an RM which meet the above-mentioned requirements are the SC1 dip method [also known as the IAP (immersion in alkaline hydrogen peroxide solution) method] [8], [9] and the spin-coating method [10]. The latter method, however, tends to cause particle formation. Another possible method is the microdrop method [7] by which a certain quantity of the RM element is deposited on a part of the surface, though the resultant specimen is not uniform.

C.2 Silicon wafer for the RM

The surface density of the contamination on the silicon wafer used as the RM is required to be less than 10^{10} atoms/cm^2. Wafers used for 16M DRAM (dynamic random-access memory) are suitable.

If the crystallographic orientation of the wafer varies, the conditions for the generation of spectral-interference peaks will vary [11]. Hence the azimuth of the chemomechanically polished or epitaxial wafer to be used should preferably be identical with that of the wafer under test.

C.3 The RM element

Transition metals with a high generation efficiency are appropriate for use as the RM element. Of such elements, Ni and Fe are recommended for the following reasons:

a) If the W-L_{II}-M_{IV} line is used as the X-ray source, there will be some overlap of the Cu peak with the escape peak of the scattered W-L_{II}-M_{IV} line. This may result in errors due to the deconvolution process.

b) If the W-L_{II}-M_{IV} line is used as the X-ray source, there will be some overlap of the Zn peak with the scattered W-L_{II}-M_{IV} line and with the Compton peaks. This may result in errors, depending how the baseline is drawn.

c) The results of the inter-laboratory test programme have shown that Fe and Ni are comparatively stable, i.e. they are deposited in the form of a uniform film and they remain within the native-oxide film [12].

d) Fe-containing airborne particles are fairly common, and when they fall onto the wafer surface or adhere to the detector window they will cause the generation of spurious peaks.

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More careful treatment of an Fe RM is therefore be required, as compared to RMs utilizing other elements, e.g. Ni. It was observed, however, by all the participants in the inter-laboratory test programme that the Fe RM was not contaminated.

e) It is not known how the use of Co, V or Mn as the RM element would affect the native-oxide film. Also, the behaviour of these elements inside or outside the native-oxide film on the silicon surface is unknown, and the precision of such RMs has not been demonstrated by inter-laboratory testing.

C.4 Procedures for preparing RMs

C.4.1 SC1 dip method [8], [9]

The wafer surface is first cleaned so as to obtain a surface contamination level of 10^{10} atoms/cm^2 or less. The wafer is then dipped in an SC1 cleaning solution (water, ammonia and hydrogen peroxide in the ratio 5 : 0,1 to 1 : 1 by volume) containing the ions of the RM element in order to deposit a certain quantity of the RM element in the native-oxide film.

It should be noted, however, that it is difficult to deposit certain elements, e.g. Ni, uniformly over the whole range of concentration of ammonia in the solution. It is therefore recommended that a 5 : 0,25 : 1 solution be used, as this provides satisfactorily uniform surface deposition.

The use of SC1 cleaning solution has the advantage that etching and formation of the native-oxide film proceed concurrently, thereby maintaining the thickness of the native-oxide film whilst allowing the impurity element in the solution to be taken up by the native-oxide film.

C.4.2 Spin-coating method [10]

The wafer surface is first cleaned so as to obtain a hydrophobic surface with a contamination level of 10^{10} atoms/cm^2 or less. A droplet of an acidic solution containing the ions of the RM element is then dispersed over the entire wafer surface. The wafer is held in this state for a certain period of time to allow the RM element to be dispersed on the silicon substrate and is then spun dry.

This method provides satisfactory uniformity of the surface contaminant. More than one element may be deposited at the same time.

C.4.3 Microdrop method [7]

The wafer surface is first cleaned so as to obtain a hydrophobic surface with a contamination level of 10^{10} atoms/cm^2 or less. A droplet of known volume of a solution containing the ions of the RM element is then deposited on the wafer surface and allowed to dry.

The surface density of the deposited element depends on its concentration in the solution and the volume of the droplet. It should be noted, however, that the intensity of the fluorescence X-rays may vary considerably depending upon the relative positions of the droplet residue and the detector [7]. The diameter of the droplet residue will also affect the intensity [12] (see annex E).

C.5 Calibration of RMs

RMs are calibrated as soon as possible after preparation.

Wafers prepared by the SC1 or the spin-coating method are calibrated by AAS, ICP-MS or some other method relevant to the RM element contained in the native-oxide film on the wafer and recovered by the VPD specimen preparation method (see annex D).

If hydrofluoric acid is used to gather the impurities, including Ni, from the oxide film, the impurities present in the acid may be a source of difficulty. Often, therefore, the native-oxide film on the wafer surface is dissolved using

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vapourized hydrofluoric acid to recover the RM element. Radioactivation analysis is also used, which avoids circumferential contamination after radioactivation, such as occurs during VPD specimen preparation and the subsequent analysis.

Rutherford backscattering and forward-scattering methods, including the method known as heavy-ion backscattering spectroscopy, can be used to calibrate RMs directly.

RMs prepared by the microdrop method do not need to be calibrated as the surface density of the deposited element can be calculated from its concentration in the solution and the volume of the droplet. A calculation procedure which gives reliable results is given in SEMI Standard M33.

C.6 Recommended RMs

The SC1 method produces RM wafers having contaminant-density levels of 10^{11} atoms/cm^2 to 10^{13} atoms/cm^2 with good surface-density and depth uniformity. The repeatability of this method is such that up to 25 practically identical specimens can be produced at the same time.

In the case of the spin-coating method, the depth distribution of the deposited element is not constant. Though this would lead to an error in the analytical results, the international inter-laboratory test programme demonstrated that specimens prepared by the spin-coating method gave satisfactory reproducibility.

The predominant problem associated with the microdrop method is that the calculation procedure for converting the solution concentration into a surface density is not yet reliably established. Also, any error in setting the coordinates would lead to a difference in the fluorescence X-ray intensity. Further errors may be introduced by the fact that the distribution of the elements on the RM and the test specimen are always different. This method is simple, however, and applicable to lower surface densities.

It is recommended that the SC1 method and the spin-coating method be used.

C.7 Storage and lifetime of RMs

RMs should be stored in the same container as the blank RM and in the same environment as the TXRF instrument.

Despite these precautions, airborne particles may be deposited on RMs during measurement.

It is probable that the native-oxide film grows and hydrocarbons are deposited on RMs during storage in the container.

It is reasonable to assess the level of contamination of the RM and the blank RM from the apparent level of contamination on the blank RM after only making a background correction. If the apparent level of contamination is greater than 10 % of the surface density of the element on the RM, the RM and the blank RM are considered to have exceeded their useful life and should be replaced. The normal life expectancy of RMs is less than 6 months.

C.8 Caution

The user should be aware that silicon surfaces can be covered by both particulate-type and film-type contamination, and that some impurity elements, e.g. Zn, can occur in both of these forms. The fluorescence X-ray intensity depends upon the physical state and the depth of the contamination. The elemental levels measured for particulate-type contamination and for the residue produced by a VPD scanning droplet will be higher than those measured if film-type RMs are used for quantification purposes. This is, however, the most reliable means of quantifying levels of contamination on unknown specimens.

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Annex D
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VPD-TXRF method

D.1 General information

The standard TXRF method is valid in the range from 10^{10} atoms/cm^2 to 10^{13} atoms/cm^2. The practical measurement range can be improved upon by the use of VPD-TXRF, with which the detection range is 5×10^8 atoms/cm^2 to 5×10^{12} atoms/cm^2. In the VPD-TXRF method, the contaminants are collected from the whole wafer surface and deposited in the form of a small residue which is then analysed by TXRF.

D.2 Collection of contamination elements

The contamination elements are collected by decomposing the native-oxide film present on the wafer surface. This may be achieved either by exposing the wafer surface to HF vapour in a VPD chamber or by scanning an HF droplet over the surface of a polished or epitaxial silicon wafer specimen.

An HF-treated surface becomes hydrophobic. Thus any droplets on the wafer surface will tend to become spherical as the contact angle between the droplets and wafer surface exceeds 1,05 rad (60°), so these droplets will gather into one droplet. Alternatively, by sandwiching one drop of HF or HF + $HN0_3$ between the container and wafer it is possible to expose the whole wafer surface simultaneously[13]. The chemicals should be of ultra-pure grade and the environment in which this operation is carried out should be ISO Class 4 or better. The droplet obtained can also be analysed by the AAS or the ICP-MS method.

NOTE Patents concerning methods of collecting contamination elements have been applied for in many countries. ISO cannot give any authoritative or comprehensive information about the existence, validity or scope of such patent rights. Users of this International Standard are expressly advised that determination of any such patent rights and the risk of infringement of such rights are entirely their own responsibility.

D.3 Producing the droplet residue

The spherical droplet is dried on the silicon wafer surface from which the contamination elements have been collected or on another wafer which has been freshly made hydrophobic. The accuracy is dependent on the size (area and height) of the residue: the smaller the size, the better the accuracy. It is well known that a hydrophobic silicon wafer strongly attracts and adsorbs airborne particles or chemicals in the cleanroom. Use of a drying chamber with a vacuum system or a flow of clean, inert gas at ambient temperature is recommended.

D.4 Measurement by TXRF

D.4.1 Size of residue

The residue is small. The artificial residue employed in the inter-laboratory test programme had a diameter of 350 µm and a height of 50 nm.

D.4.2 Finding the residue spot

It is very difficult to find the residue spot unless the precise position is recorded, the quick-search system of the TXRF instrument is used or a spot-mark is made with nitric acid.

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D.4.3 Effect of residue size

When the residue is not small, the measurement error becomes greater. In addition, salts of different metallic elements often become separated and the distribution of such elements is not homogeneous. This inhomogeneity makes the determination of multi-element contamination less accurate.

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Annex E
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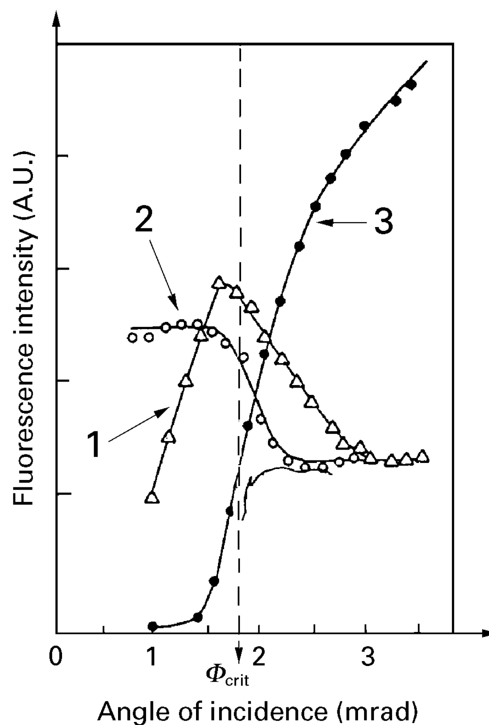
Glancing-angle settings

E.1 TXRF anglescans of ideal specimens [14]

TXRF anglescans using an Mo-K-$L_{II,III}$ X-ray source are shown in Figure E.1 for an ideal specimen consisting of a polished silicon wafer. Of particular importance is the difference in the anglescans of the particulate-type and film-type contamination, although the atomic surface density is the same in each case. At about 1 mrad (0,06°), there is a very large difference between the TXRF signals for the particulate-type and film-type contamination for the same surface density. At about 1,3 mrad (0,07°), there is no difference between the two signals. This angle is sometimes called the "crossover angle" because it is the angle at which the anglescans for the two types of contamination cross each other.

The importance of this crossover angle is clear when we consider the anglescan of an RM and that of an unknown specimen. Assume for the moment that the RM has an anglescan of the film-type form in Figure E.1. Now if the unknown specimen has an anglescan similar to the film-type curve (plated or sputtered) of Figure E.1, any angle can be used for the quantification. However, if the unknown has an anglescan similar to the particulate-type curve (residue) in Figure E.1, then only the measurement at the crossover angle gives correct quantification. If in this case the measurement is made instead at a low angle, such as 1 mrad (56 % of the theoretical critical angle), the accuracy of the quantification is in error by the ratio of the signal intensities shown in Figure E.1 at 1 mrad. In this figure, the error would be about 2,5 times. If an even lower angle were used, the error could reach five times or more.



Key

1 Plated

2 Residue

3 Bulk

Figure E.1 — Experimental curves showing the angular dependence of the fluorescence

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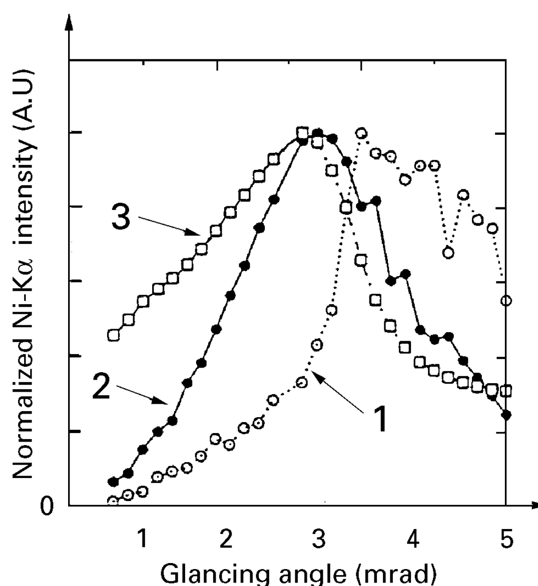
In actual analysis, it is difficult to check the anglescan of each unknown, because of the very low signal intensities at low contamination levels. Therefore, one cannot always know whether or not there is a major error in the quantification if a lower angle is used.

The only angle which ensures accurate quantification in the measurement of ideal specimens is the crossover angle, and it is therefore this angle which is recommended. In real RMs, the anglescan is sometimes not exactly like the film-type anglescan in Figure E.1, but is somewhat broader in width. In this case, the crossover point becomes a range, perhaps between 1,2 mrad (67 % of the theoretical critical angle) and 1,5 mrad (84 % of the theoretical critical angle).

E.2 Anglescan of film-type contamination [6], [15]

The depth of measurement is defined as the penetration depth at which the X-ray intensity decreases by 1/e. This depth varies with the energy of the X-rays, the glancing angle and the matrix electron density. For the silicon surface, it is less than 5 nm. The intensity of the fluorescence X-rays from each contamination element varies with the glancing angle. Figure E.2 shows the results of anglescans, using an Ni-K-$L_{II,III}$ X-ray source, of three Ni RMs made by the SC1 dip method: Ni-1 with ca. 10^{11} atoms/cm^2, Ni-2 with ca. 10^{12} atoms/cm^2 and Ni-3 with ca. 10^{14} atoms/cm^2. The anglescan curves are normalized with respect to their maximum value. The curves show the differences between the deposited-film types. Ni-3 is assumed to be particle-forming NiSi precipitates. Figure E.3 shows the results of anglescans, using an Ni-K-$L_{II,III}$ X-ray source, of Ni-3 by three laboratories. The anglescan curves are the same in each case.



Key

1 Ni-1: ca. 10^{11} atoms/cm^2

2 Ni-2: ca. 10^{12} atoms/cm^2

3 Ni-3: ca. 10^{13} atoms/cm^2

Figure E.2 — Anglescan results for RMs with different Ni surface densities

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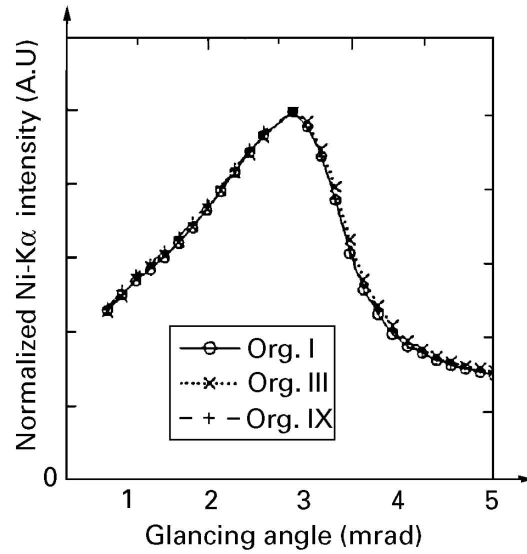

Figure E.3 — Reproducibility of anglescan intensity

E.3 Anglescans of particulate-type contamination [12]

VPD residues on the silicon surface can be several micrometres high. Thus both penetration of the residue and reflection from the silicon wafer occur. Figure E.4 shows the fluorescence intensity as a function of glancing angle for residues of various heights. For excitation at total reflection below the critical angle, different oscillations occur owing to standing waves above the specimen.

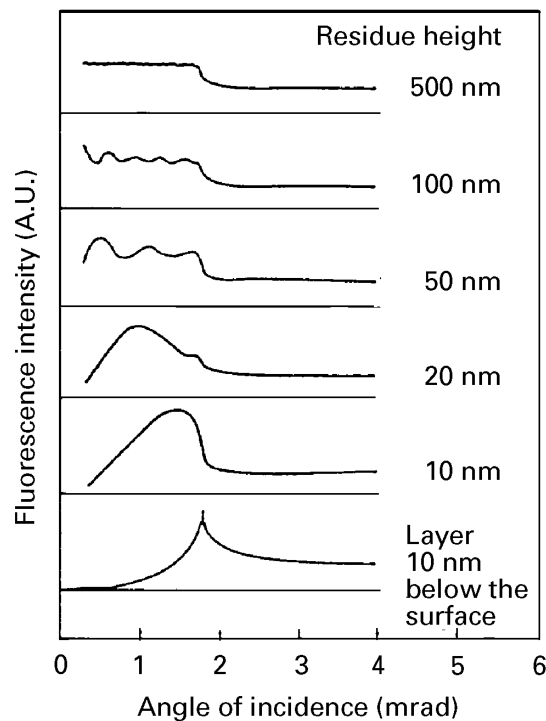

Figure E.4 — Effect of particle size

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E.4 Glancing-angle settings

For the glancing-angle setting, a higher angle is preferable, i.e. 75 % of the critical angle, because real silicon surfaces can be covered by both particulate-type and film-type contamination. For VPD-TXRF, the glancing-angle settings are the same as with conventional TXRF, although no theoretical reasons exist for this at present.

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Annex F
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International inter-laboratory test results

F.1 General

An international inter-laboratory test programme was carried out from July to September 1995 in order to obtain an estimate of the precision of the method described in this International Standard. 15 laboratories from Japan, Europe and the USA participated in the programme.

Four test specimens and one RM using silicon wafers were distributed as a set to each laboratory. Each test specimen and the RM were contained separately in individual boxes. The spoke-and-hub method of testing was used in order to reduce accidental contamination. 17 sets of measurements were obtained from the 15 laboratories.

The statistical analysis of the results was carried out in accordance with the principles of ISO 5725-2.

F.2 Test specimens and RMs

Three of the test specimens (levels 1, 2 and 3) in each set were intentionally contaminated with Ni or Fe using the SC1 dip method, and the fourth test specimen with both Fe (level 4) and Ni (level 5) on the same wafer using the microdrop method. The RM, on which Ni was deposited using the SC1 dip method, was used to prepare a calibration curve. Prior to distribution, the RM and each specimen were analysed by VPD-AAS.

All participating laboratories were informed of the atomic surface density of the contamination on the RM (Ni: $0,85 \times 10^{12}$ atoms/cm^2), but not of those on the test specimens.

Details of the contamination is given in Table F.1.

Table F.1 — Details of contamination

Level	Element	Surface density of impurity
1	Ni	$0,11 \times 10^{12}$ atoms/cm^2
2	Fe	$0,91 \times 10^{12}$ atoms/cm^2
3	Fe	$0,047 \times 10^{12}$ atoms/cm^2
4	Fe	$1,08 \times 10^{12}$ atoms (in 10 µl droplet)
5	Ni	$1,03 \times 10^{12}$ atoms (in 10 µl droplet)

F.3 TXRF analysis procedure

The RM was first measured once and a calibration curve drawn. The test specimens were measured three times a day for three days. The measurement conditions and measurement data, such as the fluorescence X-ray intensities, were recorded. These data are referred to as "determination data" hereinafter. The contaminant on the RM was Ni. The effectiveness of Fe as an RM contaminant was also studied. One test specimen on which Fe was deposited (Level 2) was used as an RM. The data obtained are referred to as "simulation data" hereinafter.

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F.4 Statistical analysis

F.4.1 General

After confirming the stability of the measurements, the absence of any accidental contamination during the measurements and the uniformity of the sets of specimens, the repeatability and reproducibility were calculated in accordance with the principles of ISO 5725-2.

F.4.2 Statistical tests for outliers

Mandel's test was applied to the data in accordance with ISO 5725-2. No data were excluded as stragglers or outliers as a result of this test. Grubb's test was also applied to the data at the 99 % confidence level in accordance with ISO 5725-2. Two results for one test specimen were excluded as outliers as a result of this test.

F.4.3 Calculation of repeatability and reproducibility

The determination data and simulation data were processed in accordance with ISO 5725-2 to obtain the repeatability and reproducibility.

F.5 Results of the statistical analysis

F.5.1 The results of the statistical analysis of the determination data are shown in Table F.2. It should be noted that the reproducibility data include errors due to unavoidable inhomogeneity of the specimens.

Table F.2 — Repeatability and reproducibility from the determination data

Level	No. of laboratories p	General mean m ($\times 10^{12}$ atoms/cm^2)	Repeatability s_r ($\times 10^{12}$ atoms/cm^2)	Reproducibility s_R ($\times 10^{12}$ atoms/cm^2)
1	15	0,105	0,015	0,037
2	17	1,026	0,120	0,272
3	17	0,094	0,017	0,036
4	15	1,454	0,121	0,897
5	14	1,370	0,106	0,811

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F.5.2 The results of the statistical analysis of the simulation data are shown in Table F.3. It should be noted that the reproducibility data include errors due to any unavoidable inhomogeneity of the specimens.

Table F.3 — Repeatability and reproducibility from the simulation data

Level	No. of laboratories p	General mean m (× 10^{12} atoms/cm^2)	Repeatability s_r (× 10^{12} atoms/cm^2)	Reproducibility s_R (× 10^{12} atoms/cm^2)
1	15	0,114	0,016	0,045
2	a	a	a	a
3	17	0,086	0,013	0,032
4	16	1,260	0,114	0,845
5	16	1,271	0,109	0,764

[a] Level 2 (Fe) specimen used as the RM.

The statistical analysis of the results using the level 2 (Fe) specimen as the RM was carried out as follows:

a) the data obtained from the Fe RM in a particular laboratory was applied only to the results from that laboratory;

b) it was assumed that the atomic surface density of the Fe on the Fe RM was 0,91 × 10^{12} atoms/cm^2;

c) the relative sensitivity factor was calculated between the determination data from the Ni RM and those from the Fe RM;

d) each calibration curve was prepared by calculating the mean of the three values of the intensity of the fluorescence X-rays from the Fe RM on each of the three measurement days;

e) each calibration curve was then used to determine the atomic surface density of the contamination at levels 1, 3, 4 and 5.

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