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Surface chemical analysis — Chemical methods for the collection of elements from the surface of silicon-wafer working reference materials and their determination by total-reflection X-ray fluorescence (TXRF) spectroscopy

Analyse chimique des surfaces — Méthodes chimiques pour collecter les éléments analysés de tranches de silicium comme matériaux de référence pour l'analyse par spectroscopie de fluorescence X en réflexion totale (TXRF)

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Contents

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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights (see Note to 10.1). ISO shall not be held responsible for identifying any or all such patent rights.

ISO 17331 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*.

Introduction

The measurement of metal impurities on the surface of silicon wafers by total-reflection X-ray fluorescence spectroscopy (TXRF) is commonly accepted by the semiconductor industry.

ISO 14706 specifies a TXRF method for the measurement of metal impurities on a silicon-wafer surface with atomic surface densities from 1×10^{10} atoms/cm^2 to 1×10^{14} atoms/cm^2, also a vapour-phase decomposition (VPD) method for atomic surface densities from 5×10^{8} atoms/cm^2 to 5×10^{12} atoms/cm^2.

In ultra-large-scale integrated circuit (ULSI) manufacturing, the measurement of very-low-level metal impurities on the surface of a silicon wafer, less than 10^{10} atoms/cm^2, is currently required.

Reference materials with low-level metal impurities are important in TXRF analysis (see ISO 14706), but the reference materials have a limited shelf life, especially as regards surface contamination. As a result, preparation methods for working reference materials need to be standardized.

This test method allows the calculation of metal impurities on the surface of reference and test wafers. Interlaboratory trials in nine laboratories in different countries indicated that this method has good reproducibility and repeatability.

Surface chemical analysis — Chemical methods for the collection of elements from the surface of silicon-wafer working reference materials and their determination by total-reflection X-ray fluorescence (TXRF) spectroscopy

1 Scope

This International Standard specifies chemical methods for the collection of iron and/or nickel from the surface of silicon-wafer working reference materials by the vapour-phase decomposition method or the direct acid droplet decomposition method.

NOTE The determination of the elements collected may be carried out by graphite-furnace atomic-absorption spectroscopy or inductively coupled plasma mass spectrometry instead of by total-reflection X-ray fluorescence spectroscopy.

This International Standard applies to iron and/or nickel atomic surface densities from 6×10^9 atoms/cm^2 to 5×10^{11} atoms/cm^2.

2 Normative references

The following referenced documents are indispensable for the application 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 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 14644-1:1999, *Cleanrooms and associated controlled environments — Part 1: Classification of air cleanliness*

ISO 14706:2000, *Surface chemical analysis — Determination of surface elemental contamination on silicon wafers by total-reflection X-ray fluorescence (TXRF) spectroscopy*

3 Terms and definitions

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

3.1

working reference material

silicon wafer used for the calibration specified in ISO 14706

3.2

calibration specimen

silicon wafer with a known amount of iron and/or nickel in a dried residue, used for calibration purposes

3.3
calibration solution
solution used to make a calibration specimen

3.4
internal standard
known amount of vanadium or scandium used to normalize the variation in the fluorescence X-ray intensities of iron and/or nickel in a residue

3.5
internal-standard solution
solution used to make an internal standard

3.6
scanning
rolling a VPD or DADD microdroplet on a hydrophobic silicon surface in a reproducible pattern to cover the entire surface of the wafer

4 Abbreviations

For the purposes of this document, the following abbreviations apply:

TXRF	total-reflection X-ray fluorescence spectroscopy
VPD	vapour-phase decomposition
DADD	direct acid droplet decomposition
PE	polyethylene
PFA	polyfluoroalkoxyethylene
PP	polypropylene
PTFE	polytetrafluoroethylene
GF-AAS	graphite furnace atomic absorption spectroscopy
ICP-MS	inductively coupled plasma mass spectroscopy

5 Reagents

WARNING — Hydrofluoric acid is a highly corrosive liquid which attacks glass and has a great affinity for water. Its vapour is irritant and toxic. Its action on the skin and eyes is strongly corrosive, producing severe and painful burns which may not be immediately evident and which respond slowly to treatment.

All specimens shall be handled in a well-ventilated area. Rubber gloves, rubber boots and a gown of a suitable size to give adequate protection to the individual, as well as full head and face protection, shall be worn when handling materials.

In an event of contact or suspected contact with hydrofluoric acid, wash the affected area with copious quantities of water and seek immediate medical attention. Consult the manufacture's literature for further information.

5.1 Ultra-pure water, containing less than 1 pg/ml of each of the impurities iron, nickel, vanadium and scandium.

5.2 Ultra-pure hydrofluoric acid, concentration ca. 21 mol/l to ca. 29 mol/l and containing less than 10 pg/ml of each of the impurities iron, nickel, vanadium and scandium.

NOTE The concentration of commercially available ultra-pure hydrofluoric acid is expressed as a percentage. 21 mol/l hydrofluoric acid corresponds to ca. 38 % and 29 mol/l to ca. 50 %.

5.3 Ultra-pure hydrogen peroxide, concentration ca. 10 mol/l to ca. 12 mol/l and containing less than 10 pg/ml of each of the impurities iron, nickel, vanadium and scandium.

NOTE The concentration of commercially available ultra-pure hydrogen peroxide is expressed as a percentage. 10 mol/l hydrogen peroxide corresponds to ca. 30 % and 12 mol/l to ca. 35 %.

5.4 Ultra-pure nitric acid, concentration ca. 11 mol/l to ca. 15 mol/l and containing less than 100 pg/ml of each of the impurities iron, nickel, vanadium and scandium.

NOTE The concentration of commercially available ultra-pure nitric acid is expressed as a percentage. 11 mol/l nitric acid corresponds to ca. 55 % and 15 mol/l to ca. 68 %.

5.5 Hydrofluoric acid, concentration ca. 29 mol/l and containing less than 100 pg/ml of each of the impurities iron, nickel, vanadium and scandium.

NOTE The concentration of commercially available hydrofluoric acid is expressed as a percentage. 29 mol/l hydrofluoric acid corresponds to ca. 50 %. The hydrofluoric acid specified in 5.5 is available commercially as “semiconductor” grade.

5.6 Hydrogen peroxide, concentration ca. 10 mol/l and containing less than 100 pg/ml of each of the impurities iron, nickel, vanadium and scandium.

NOTE The concentration of commercially available hydrogen peroxide is expressed as a percentage. 10 mol/l hydrogen peroxide corresponds to ca. 30 %. The hydrogen peroxide specified in 5.6 is available commercially as “semiconductor” grade.

5.7 Standard solutions

5.7.1 Iron standard solution: Use a commercially available 1 000 µg/ml iron standard solution specified for AAS.

5.7.2 Nickel standard solution: Use a commercially available 1 000 µg/ml nickel standard solution specified for AAS.

5.7.3 Vanadium standard solution: Use a commercially available 1 000 µg/ml vanadium standard solution specified for AAS.

5.7.4 Scandium standard solution: Use a commercially available 1 000 µg/ml scandium standard solution specified for AAS.

5.8 Diluted calibration solutions

5.8.1 Diluted iron calibration solution 1: A 10 µg/ml iron calibration solution in nitric acid.

Prepare diluted iron calibration solution 1 by either method a) or b) below:

a) Transfer 1 000 µl of iron standard solution (5.7.1) to a plastic 100 ml one-mark volumetric flask (6.1) with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca.1 ml of ultra-pure nitric acid (5.4) and finally make up to the mark with ultra-pure water (5.1) and mix.

b) Weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 1 000 µl of iron standard solution (5.7.1) to the beaker with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally add ultra-pure water (5.1) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

5.8.2 Diluted iron calibration solution 2: A 100 ng/ml iron calibration solution in nitric acid.

Prepare diluted iron calibration solution 2 by either method a) or b) below:

a) Transfer 1 000 µl of diluted iron calibration solution 1 (5.8.1 a) to a plastic 100 ml one-mark volumetric flask (6.1) with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally make up to the mark with ultra-pure water (5.1) and mix.

b) Weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 1 000 µl of diluted iron calibration solution 1 (5.8.1 b) to the beaker with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally add ultra-pure water (5.1) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

5.8.3 Diluted nickel calibration solution 1: A 10 µg/ml nickel calibration solution in nitric acid.

Prepare diluted nickel calibration solution 1 by either method a) or b) below:

a) Transfer 1 000 µl of nickel standard solution (5.7.2) to a 100 ml one-mark volumetric plastic flask (6.1) with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally make up to the mark with ultra-pure water (5.1) and mix.

b) Weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 1 000 µl of the nickel standard solution (5.7.2) to the beaker with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally add ultra-pure water (5.1) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

5.8.4 Diluted nickel calibration solution 2: A 100 ng/ml nickel calibration solution in nitric acid.

Prepare diluted nickel calibration solution 2 by either method a) or b) below:

a) Transfer 1 000 µl of diluted nickel calibration solution 1 (5.8.3 a) to a plastic 100 ml one-mark volumetric flask (6.1) with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally make up to the mark with ultra-pure water (5.1) and mix.

b) Weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 1 000 µl of diluted nickel calibration solution 1 (5.8.3 b) to the beaker with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally add ultra-pure water (5.1) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

5.8.5 Diluted iron and nickel mixture calibration solution 1: A 10 µg/ml iron and 10 µg/ml nickel mixture calibration solution in nitric acid.

Prepare diluted iron and nickel mixture calibration solution 1 by either method a) or b) below:

a) Transfer 1 000 µl of iron standard solution (5.7.1) and 1 000 µl of nickel standard solution (5.7.2) to a plastic 100 ml one-mark volumetric flask (6.1) using a different plastic micropipette (6.2) for each, add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally make up to the mark with ultra-pure water (5.1) and mix.

b) Weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 1 000 µl of iron standard solution (5.7.1) and 1 000 µl of nickel standard solution (5.7.2) to the beaker using a different plastic micropipette (6.2) for each, add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally add ultra-pure water (5.1) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

5.8.6 Diluted iron and nickel mixture calibration solution 2: A 100 ng/ml iron and 100 ng/ml nickel mixture calibration solution in nitric acid.

Prepare diluted iron and nickel mixture calibration solution 2 by either method a) or b) below:

a) Transfer 1 000 µl of diluted iron and nickel mixture calibration solution 1 (5.8.5 a) to a plastic 100 ml one-mark volumetric flask (6.1) with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally make up to the mark with ultra-pure water (5.1) and mix.

b) Weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 1 000 µl of iron and nickel mixture calibration solution 1 (5.8.5 b) to the beaker with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally add ultra-pure water (5.1) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

5.9 Internal standard solution: A 1 µg/ml vanadium or scandium solution in nitric acid.

Prepare the internal standard solution by either method a) or b) below:

a) Transfer 100 µl of vanadium standard solution (5.7.3) or 100 µl of scandium standard solution (5.7.4) to a plastic 100 ml one-mark volumetric flask (6.1) with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally make up to the mark with ultra-pure water (5.1) and mix.

b) Weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 100 µl of vanadium standard solution (5.7.3) or 100 µl of scandium standard solution (5.7.4) to the beaker with a plastic micropipette (6.2), add ca. 90 ml of ultra-pure water (5.1), then add ca. 1 ml of ultra-pure nitric acid (5.4) and finally add ultra-pure water (5.1) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

5.10 Blank solution: A mixture containing ca. 1 mol/l of hydrofluoric acid and ca. 0,7 mol/l of hydrogen peroxide.

Prepare the blank solution by either method a) or b) below:

a) Transfer ca. 50 ml of ultra-pure hydrofluoric acid (5.2) and ca. 60 ml of ultra-pure hydrogen peroxide (5.3) to a plastic 1 000 ml one-mark volumetric flask (6.1), make up to the mark with ultra-pure water (5.1) and mix.

b) Weigh a 1 000 ml plastic beaker (6.3) to the nearest 1 g. Transfer ca. 56 g of ultra-pure hydrofluoric acid (5.2) and ca. 65 g of ultra-pure hydrogen peroxide (5.3) to the beaker, add ultra-pure water (5.1) to make the mass up to 1 000 g (plus the mass of the beaker) to the nearest 1 g and mix.

5.11 Scanning solution: A mixture containing 1 mol/l of hydrofluoric acid and 0,7 mol/l of hydrogen peroxide plus 25 ng/ml of vanadium or scandium internal standard.

Prepare the scanning solution by either method a) or b) below:

a) Transfer ca. 5,0 ml of ultra-pure hydrofluoric acid (5.2) and ca. 6,0 ml of ultra-pure hydrogen peroxide (5.3) to a plastic 100 ml one-mark volumetric flask (6.1), then add 2 500 µl of vanadium or scandium internal standard solution (5.9 a) with a plastic micropipette (6.2), make up to the mark with ultra-pure water (5.1) and mix.

b) Weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer ca. 5,6 g of ultra-pure hydrofluoric acid (5.2) and ca. 6,5 g of ultra-pure hydrogen peroxide (5.3) to the beaker, then add 2 500 µl of vanadium or scandium internal standard solution (5.9 b) with a plastic micropipette (6.2), add ultra-pure water (5.1) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

5.12 Cleaning solution: A mixture containing ca. 5 mol/l of hydrofluoric acid and ca. 2 mol/l of hydrogen peroxide.

Prepare the cleaning solution using hydrofluoric acid (5.5) and hydrogen peroxide (5.6). Mix the hydrofluoric acid and hydrogen peroxide with ultra-pure water (5.1) in the approximate volume ratio of 1:1:3.

6 Apparatus

For the preparation of reagents and specimens use ordinary laboratory glassware or plasticware unless otherwise stated.

In order to check the accuracy of micropipettes used in the volumetric method, these shall be periodically calibrated by taking an exact volume of water with the micropipette and weighing it on a high-precision balance.

CAUTION — Apparatus that may come into contact with hydrofluoric acid and/or hydrofluoric acid solution shall not be made of glass or other silicate materials. Hydrofluoric acid attacks such materials.

6.1 Plastic one-mark volumetric flasks, 100 ml ± 1 ml and 1 000 ml ± 1 ml, made of PE, PFA or PP.

6.2 Plastic micropipettes, 100 µl ± 1 µl, 1 000 µl ± 10 µl, from 10 µl ± 0,1 µl to 100 µl ± 1 µl and from 100 µl ± 1 µl to 1 000 µl ± 10 µl, made of PE, PFA or PP.

6.3 Plastic beakers, 100 ml and 1 000 ml, made of PE, PFA, PP or PTFE.

6.4 Wafer-stand, made of PFA or PTFE.

6.5 Drying apparatus: Use either an infrared lamp with a power controller or a vacuum vessel fitted with gas flow equipment and/or an infrared lamp.

6.6 Vertical laminar flow cabinet, meeting the requirements for ISO class 2 (see ISO 14644-1) or better. For reasons of cleanliness and operator safety, clean air shall be passed over the specimen-handling area and exhausted outside the cabinet.

6.7 VPD box, made of PTFE, PFA or similar material.

7 Specimen preparation and specimen measurement environments

7.1 Specimens shall be handled in a clean environment (ISO class 4 or better) (see ISO 14644-1).

7.2 The instruments shall be set up in a clean environment (ISO class 5 or better) (see ISO 14644-1).

8 Preparation of calibration specimens

8.1 Prepare five silicon wafers of which the crystallographic orientation is the same as that of the silicon wafers specified in ISO 14706.

Just before preparing the actual calibration specimens, clean the silicon wafers with cleaning solution (5.12) in order to make the surface of the wafers clean and hydrophobic.

8.2 Prepare calibration solutions containing 0 ng/ml, 0,1 ng/ml, 1 ng/ml, 10 ng/ml and 25 ng/ml of iron, nickel, or iron and nickel, plus 25 ng/ml of vanadium or scandium internal standard solution (5.9) by either the volumetric procedure in 8.2.1 or the gravimetric procedure in 8.2.2.

8.2.1 Volumetric method

Prepare five plastic 100 ml one-mark volumetric flasks (6.1) for the following solutions:

a) For the preparation of the 0 ng/ml calibration solution, transfer 2 500 µl of vanadium or scandium internal standard solution (5.9 a) with a plastic micropipette (6.2) to a plastic 100 ml one-mark volumetric flask (6.1), make up to the mark with blank solution (5.10 a) and mix.

b) For the preparation of the 0,1 ng/ml calibration solution, transfer 100 µl of diluted iron calibration solution 2 (5.8.2 a), diluted nickel calibration solution 2 (5.8.4 a) or diluted iron and nickel mixture calibration solution 2 (5.8.6 a) with a plastic micropipette (6.2) to a plastic 100 ml one-mark volumetric flask (6.1) and add 2 500 µl of vanadium or scandium internal standard solution (5.9 a), also with a plastic micropipette (6.2), make up to the mark with blank solution (5.10 a) and mix.

c) For the preparation of the 1 ng/ml calibration solution, transfer 1 000 µl of diluted iron calibration solution 2 (5.8.2 a), diluted nickel calibration solution 2 (5.8.4 a) or diluted iron and nickel mixture calibration solution 2 (5.8.6 a) with a plastic micropipette (6.2) to a plastic 100 ml one-mark volumetric flask (6.1) and add 2 500 µl of vanadium or scandium internal standard solution (5.9 a), also with a plastic micropipette (6.2), make up to the mark with blank solution (5.10 a) and mix.

d) For the preparation of the 10 ng/ml calibration solution, transfer 100 µl of diluted iron calibration solution 1 (5.8.1 a), diluted nickel calibration solution 1 (5.8.3 a) or diluted iron and nickel mixture calibration solution 1 (5.8.5 a) with a plastic micropipette (6.2) to a plastic 100 ml one-mark volumetric flask (6.1) and add 2 500 µl of vanadium or scandium internal standard solution (5.9 a), also with a plastic micropipette (6.2), make up to the mark with blank solution (5.10 a) and mix.

e) For the preparation of the 25 ng/ml calibration solution, transfer 250 µl of diluted iron calibration solution 1 (5.8.1 a), diluted nickel calibration solution 1 (5.8.3 a) or diluted iron and nickel mixture calibration solution 1 (5.8.5 a) with a plastic micropipette (6.2) to a 100 ml plastic one-mark volumetric flask (6.1) and add 2 500 µl of vanadium or scandium internal standard solution (5.9 a), also with a plastic micropipette (6.2), make up to the mark with blank solution (5.10 a) and mix.

NOTE Vanadium or scandium internal standard can either be added in the calibration solution, as above, or be added directly to the droplet placed on the wafer, before the droplet is dried.

8.2.2 Weighing method

Prepare five 100 ml plastic beakers (6.3) for the following solutions:

a) For the preparation of the 0 ng/ml calibration solution, weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 2 500 µl of vanadium or scandium internal standard solution (5.9 b) with a plastic micropipette (6.2) to the beaker, add blank solution (5.10 b) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

b) For the preparation of the 0,1 ng/ml calibration solution, weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 100 µl of diluted iron calibration solution 2 (5.8.2 b), diluted nickel calibration solution 2 (5.8.4 b) or diluted iron and nickel mixture calibration solution 2 (5.8.6 b) with a plastic micropipette (6.2) to the beaker, add 2 500 µl of vanadium or scandium internal standard solution (5.9 b), also with a plastic micropipette (6.2), and finally add blank solution (5.10 b) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

c) For the preparation of the 1 ng/ml calibration solution, weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 1 000 µl of diluted iron calibration solution 2 (5.8.2 b), diluted nickel calibration solution 2 (5.8.4 b) or diluted iron and nickel mixture calibration solution 2 (5.8.6 b) with a plastic micropipette (6.2) to the beaker, add 2 500 µl of vanadium or scandium internal standard solution (5.9 b), also with a plastic micropipette (6.2), and finally add blank solution (5.10 b) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

d) For the preparation of the 10 ng/ml calibration solution, weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 100 µl of diluted iron calibration solution 1 (5.8.1 b), diluted nickel calibration solution 1

(5.8.3 b) or diluted iron and nickel mixture calibration solution 1 (5.8.5 b) with a plastic micropipette (6.2) to the beaker, add 2 500 µl of vanadium or scandium internal standard solution (5.9 b), also with a plastic micropipette (6.2), and finally add blank solution (5.10 b) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

e) For the preparation of the 25 ng/ml calibration solution, weigh a 100 ml plastic beaker (6.3) to the nearest 0,1 g. Transfer 250 µl of diluted iron calibration solution 1 (5.8.1 b), diluted nickel calibration solution 1 (5.8.3 b) or diluted iron and nickel mixture calibration solution 1 (5.8.5 b) with a plastic micropipette (6.2) to the beaker, add 2 500 µl of the vanadium or scandium internal standard solution (5.9 b), also with a plastic micropipette (6.2), and finally add blank solution (5.10 b) to make the mass up to 100 g (plus the mass of the beaker) to the nearest 0,1 g and mix.

NOTE Vanadium or scandium internal standard can either be added in the calibration solution, as above, or be added directly to the droplet placed on the wafer, before the droplet is dried.

8.3 Using a plastic micropipette (6.2), place a 100 µl droplet of each calibration solution prepared in 8.2 near the centre of the surface of one of the silicon wafers prepared in 8.1. Do not place more than one droplet on each wafer.

8.4 Dry the droplet on each wafer in the drying apparatus (6.5) in the laminar-flow cabinet (6.6). The iron and/or nickel and the vanadium or scandium remain on the surface of each silicon wafer as a residue.

Throughout the drying process, explosion of the droplet or spreading out of the residue shall be avoided by optimizing the drying conditions, such as the infrared lamp power, the degree of vacuum and the evacuation rate, the gas flow rate, the drying time, etc.

If drying is carried out at atmospheric pressure in air, the drying time shall be less than 60 min.

NOTE Long drying times may make the surface hydrophilic and cause the residue to spread out.

9 Plotting the calibration curve

9.1 General

All calibration specimens prepared by the procedure specified in Clause 8 shall be measured using a TXRF apparatus in accordance with Clause 6 of ISO 14706:2000.

All calibration specimens shall be measured as described below, using the same measurement conditions throughout a series of related measurements.

9.2 Find the centre of the residue, i.e. the point where the intensity of the fluorescence X-rays from the internal standard element is estimated to be the highest.

NOTE Even if the measurement position is a short distance away from the real centre, the intensity of the signal produced by the element can be corrected using the internal standard. Therefore, a few millimetres error is usually acceptable.

9.3 Set the TXRF apparatus measurement conditions in accordance with Subclause 10.1 of ISO 14706:2000.

9.4 Measure the intensity of the fluorescence X-rays generated by the residue, and determine the integrated intensity using either procedure a) or b) below:

a) Smooth the measured digital quantities by a numerical treatment. Then determine the integrated intensity of the fluorescence X-rays by subtracting the area under the baseline.

b) Obtain the Gaussian function that best fits the measured digital quantities. Then determine the integrated intensity from the peak height and the half-width of the Gaussian function.

9.5 Correct the integrated intensity of the fluorescence X-rays of iron and/or nickel by the following equation:

$$I_{\mathrm{s},i} = F_{\mathrm{s},i} \times \frac{F_0}{F_{\mathrm{a},i}} \tag{1}$$

where

$I_{\mathrm{s},i}$ is the corrected intensity of the signal from the iron or nickel in calibration specimen i, expressed in counts per second (cps);

$F_{\mathrm{s},i}$ is the original intensity of the signal from the iron or nickel in calibration specimen i, expressed in counts per second (cps);

F_0 is an arbitrary positive numerical value to normalize the intensity of the signal from the iron or nickel in the calibration specimen, expressed in counts per second (cps);

$F_{\mathrm{a},i}$ is the intensity of the signal from the internal standard element in calibration specimen i, expressed in counts per second (cps).

NOTE Any positive value is acceptable for F_0 as long as it remains the same throughout the whole determination procedure in Clauses 9 and 11. Typically, F_0 may be the intensity of the signal from the internal standard on the calibration specimen measured first or the average intensity of the signal from the internal standard on the series of calibration specimens, etc.

9.6 Calculate the atomic surface density of iron and/or nickel on each calibration specimen, $C_{\mathrm{s},i}$, by the following equation:

$$C_{\mathrm{s},i} = \frac{m_i \times 10^{-9} \times 6{,}022 \times 10^{23}}{M \times S} \tag{2}$$

where

$C_{\mathrm{s},i}$ is the atomic surface density of iron or nickel on calibration specimen i, expressed in atoms per square centimetre (atoms/cm^2);

m_i is the mass of added iron or nickel on each calibration specimen, expressed in nanograms (ng);

M is the atomic weight of iron (55,85) or nickel (58,69);

S is the surface area of the reference material, expressed in square centimetres (cm^2).

NOTE 1 m_i will be 0 ng, 0,01 ng, 0,1 ng, 1 ng and 2,5 ng when the procedures in Clause 8 are followed accurately.

NOTE 2 In the case of the VPD method specified in 10.2, S depends on the effective scanned area determined by the collection procedure. In the case of the DADD method specified in 10.3, S is equal to the surface area of the reference material (e.g. 314 cm^2 for a 200 mm notched wafer, 707 cm^2 for a 300 mm wafer).

NOTE 3 When the wafers for the calibration specimen and the reference material are different sizes, S is still taken to be the surface area of the reference material.

9.7 Obviously erroneous data shall be investigated and corrected or discarded before carrying out the regression calculation (see ISO 5725-2:1994, Subclauses 7.2.4 and 7.2.6).

9.8 Obtain a linear regression equation by conducting the linear least-squares method on the five sets of values obtained for $I_{\mathrm{s},i}$ and $C_{\mathrm{s},i}$.

Consider the atomic surface density (in atoms/cm^2) as ordinates and the corrected integrated intensity of the fluorescence X-rays (in cps) as abscissae in the regression calculation, expressing the equation as follows:

$$C = I \times a + b \tag{3}$$

where

C is the atomic surface density of the iron or nickel on the calibration specimen, expressed in atoms per square centimetre (atoms/cm^2);

I is the corrected intensity of the signal from the iron or nickel on the calibration specimen, expressed in counts per second (cps);

a is the slope of the calibration curve for iron or nickel, expressed in atoms per square centimetre per counts per second [(atoms/cm^2)/cps];

b is the intercept of the calibration curve on the ordinate axis, expressed in atoms per square centimetre (atoms/cm^2).

10 Collection of iron and/or nickel from working reference materials

10.1 General

Iron and/or nickel shall be collected from the surface of working reference materials specified in ISO 14706 by either the VPD method (see 10.2) or the DADD method (see 10.3).

NOTE Patents concerning methods of collecting analyte elements from the surface of a silicon wafer 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.

10.2 VPD method

10.2.1 Decomposition of silicon oxide

Place a working reference material on the wafer-stand (6.4) in the VPD box (6.7) containing freshly prepared hydrofluoric acid (5.5) in a plastic beaker (6.3).

Close the VPD box and decompose the native oxide layer on the specimen with hydrofluoric acid vapour.

The decomposition time shall be from 5 min to 30 min.

NOTE The thickness of the native silicon oxide layer is ca. 1 nm. This will normally decompose in a few minutes. Too long decomposition times may cause roughening of the wafer surface.

10.2.2 Scanning and drying

After decomposition of the silicon oxide, place a 100 µl droplet of scanning solution (5.11) on the surface of the working reference material with a plastic micropipette (6.2).

Scan the surface with the droplet in a reproducible pattern, covering the entire surface in order to ensure complete collection of the iron and/or nickel.

The scanning may be done manually or by an automatic scanning machine.

After scanning, dry the entire droplet as specified in 8.4. The collected iron and/or nickel remains on the surface as a residue.

NOTE 1 An automatic scanning machine is preferable as it gives better repeatability and reproducibility.

NOTE 2 The collected iron and/or nickel may be determined by GF-AAS or ICP-MS. In this case, the volume of the scanning solution can be between 0,1 ml and 0,5 ml and the drying procedure is not required.

NOTE 3 Vanadium or scandium internal standard can either be added in the scanning solution, as above, or be added directly to the droplet placed on the wafer before the droplet is dried.

10.3 DADD method

The following DADD method for the collection of iron and/or nickel may be used instead of the VPD method.

Place a working reference material on the wafer-stand (6.4) in the laminar-flow cabinet (6.6).

Place a 100 µl droplet of scanning solution (5.11) on the surface of the reference material with a plastic micropipette (6.2).

The droplet will move across the surface by itself due to the decomposition reaction between the silicon oxide and the hydrofluoric acid. Once the droplet has stopped, scan the surface with the droplet in a reproducible pattern, covering the entire surface in order to ensure complete collection of the iron and/or nickel.

The scanning may be done manually or by an automatic scanning machine.

After scanning, dry the entire droplet as specified in 8.4. The collected iron and/or nickel remains on the surface as a residue.

NOTE NOTES 1, 2 and 3 to Subclause 10.2.2 are also applicable to the DADD method.

11 Determination of the iron and/or nickel collected from the working reference material

11.1 Measure the integrated intensity of the fluorescence X-rays generated by the collected iron and/or nickel as well as the vanadium or scandium on the working reference material and obtain the corrected integrated intensity of the iron and/or nickel fluorescence X-rays, $I_{\mathrm{m},j}$, by Equation (1).

11.2 Determine the atomic surface density of the iron and/or nickel of the working reference material, $C_{\mathrm{m},j}$, by Equation (4).

$$C_{\mathrm{m},j} = I_{\mathrm{m},j} \times a + b \tag{4}$$

where

$C_{\mathrm{m},j}$ is the atomic surface density of iron or nickel on working reference material j, expressed in atoms per square centimetre (atoms/cm^2);

$I_{\mathrm{m},j}$ is the corrected integrated intensity of the fluorescence of the iron or nickel on working reference material j obtained in 9.5, expressed in counts per second (cps).

12 Precision

An international inter-laboratory test programme based on the method specified in this International Standard was carried out by 11 laboratories in Japan, Europe and the USA. Seven test specimen groups (levels of atomic surface density of iron and nickel) were distributed as one set.

One test specimen group consisted of four silicon wafers. Nine sets of measurements were obtained from nine laboratories.

The repeatability and the reproducibility were calculated in accordance with the principles of ISO 5725-2. A statistical report of the inter-laboratory test programme is given in Annex A.

13 Test report

The test report shall include following:

a) all information necessary for the identification of the specimens, the apparatus, the laboratory and the date of analysis;

b) the class of clean environment used for specimen preparation and measurement; e.g. preparation: ISO class 4, measurement: ISO class 5

c) the specimen preparation method used; e.g. VPD

d) details of all reagents used; e.g. water: impurity less than 1 pg per millilitre

e) each element and the amount of that element found on the calibration specimens; e.g. iron, 10 pg, 1 000 pg

f) the element and the final amount of that element in the internal standard; e.g. vanadium, 2 500 pg

g) the drying conditions used when preparing the calibration specimens; e.g. infrared lamp, in air, 30 min

h) the method of scanning used; e.g. automatic scanning machine

i) the decomposition time of the silicon oxide; e.g. 10 min

j) the calibration curve; e.g. a and b in Equation (3)

k) the results of the measurements on the working reference materials;

l) any unusual feature noted during the analysis;

m) details of any operation not specified in this International Standard, as well as details of any optional operation which may have influenced the results.

Annex A
(informative)

Results of international inter-laboratory test programme

A.1 Introduction

An international inter-laboratory test programme was carried out from March to June 2000 in order to estimate the precision of this method. Eleven laboratories in Japan, Europe and the USA participated in the programme.

Each specimen group (level) consisted of four silicon wafers having the same amount of Fe and Ni. Seven test specimen groups were distributed as one set to each laboratory.

Testing was carried out using “hub-and-spoke” techniques in order to reduce accidental contamination. Nine sets of measurements were obtained from nine laboratories. The data from two laboratories could not be accepted because the data were incomplete.

Statistical analysis of the measurement results was performed in accordance with ISO 5725-2.

A.2 Test specimens

Silicon wafers of three levels (1, 2 and 5) were used as blank specimens. Level 1 was the starting material used to prepare the other levels, level 2 was a blank specimen immersed in SC 1 solution (standard cleaning solution 1, consisting of water, ammonia and hydrogen peroxide), and level 5 was a blank specimen for use with specimens prepared by spin coating. The specimens of the latter two levels (2 and 5) were prepared by immersion in SC 1 solution or by spin coating, respectively, without adding Fe or Ni. Fe and Ni were used as intentional contamination elements when preparing level 3 and level 4 specimens by immersion in SC 1, and when preparing level 6 and level 7 specimens by spin coating.

A list of these specimens is shown in Table A.1.

Table A.1 — Test specimens

Level	Type of specimen	Target density of intentional contamination with Fe and Ni
1	Starting material for all specimens	No chemical treatment
2	Blank specimen for levels 3 and 4	Treated with SC 1, but no intentional contamination
3	Specimen prepared using SC 1	5×10^{10} atoms/cm^2
4	Specimen prepared using SC 1	1×10^{11} atoms/cm^2
5	Blank specimen for levels 6 and 7	Treated by spin coating, but no intentional contamination
6	Specimen prepared by spin coating	5×10^{10} atoms/cm^2
7	Specimen prepared by spin coating	1×10^{11} atoms/cm^2

A.3 Procedure for collection and determination of contamination elements

The Fe and Ni on the test specimens were collected in accordance with Clause 10 and determined in accordance with Clause 11.

A.4 Statistical analysis

A.4.1 General

After confirmation of measurement stability, the absence of additional accidental contamination during the measurements and the uniformity of the specimen sets, the repeatability and the reproducibility were calculated in accordance with ISO 5725-2.

A.4.2 Statistical tests for outliers

Mandel's, Cochran's and Grubb's tests specified in ISO 5725-2 were applied to all reported measurement data at the 99 % confidence level. Table A.2 shows the number of specimens remaining after excluding outliers.

Table A.2 — Number of specimens remaining after exclusion of outliers

Laboratory	**Number of specimens after exclusion of outliers**													
	Fe							**Ni**						
	Level							**Level**						
	1	**2**	**3**	**4**	**5**	**6**	**7**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
1	4	4	4	3	4	4	4	4	4	4	4	4	4	4
2	4	4	4	4	4	3	4	4	4	4	4	4	4	4
3	2	2	2	2	2	2	2	2	2	2	2	2	2	2
4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
5	4	4	4	4	4	4	4	4	4	4	4	4	4	4
6	4	4	3	3	4	4	4	4	4	3	4	4	3	4
7	3	3	3	4	3	4	4	4	4	4	4	4	4	4
8	4	4	4	4	4	4	4	4	4	4	4	4	4	4
9	3	3	4	4	3	3	4	4	4	4	4	4	3	4

NOTE 1 Data from blank specimens of levels 1, 2 and 5 were excluded if the Fe or Ni density was above 1 × 10^{10} atoms/cm^2.

NOTE 2 Laboratory 3 analysed only two of the four specimens at each level using the method specified in this International Standard. The other two specimens were analysed by other methods.

A.4.3 Calculation of repeatability and reproducibility

All data after the exclusion of outliers were processed in accordance with ISO 5725-2 in order to obtain the repeatability and reproducibility of the method.

A.5 Results of statistical analysis

When calculating statistical data, the level 1 measurements from each laboratory were used as blank data for the level 2 and level 5 measurements from that laboratory. Level 2 and level 5 were also used as blank data for levels 3 and 4 and levels 6 and 7, respectively, for each laboratory.

The results of the statistical analysis of the reported measurement data are shown in Table A.3.

It should be noted that the repeatability and the reproducibility data include errors due to any unavoidable inhomogeneity of the specimens.

Table A.3 — Repeatability and reproducibility of reported measurement data after exclusion of outliers

Level		**Number of laboratories** p	**General mean** m × 10^{10} atoms/cm^2	**Repeatability** s_r × 10^{10} atoms/cm^2	**Reproducibility** s_R × 10^{10} atoms/cm^2
Fe	1	9	0,190	0,112	0,214
	2	9	–0,009	0,056	0,104
	3	9	11,51	0,629	1,353
	4	9	27,46	0,880	2,652
	5	9	0,002	0,097	0,105
	6	9	5,351	0,350	0,729
	7	9	9,873	0,346	1,090
Ni	1	9	0,042	0,026	0,034
	2	9	–0,007	0,025	0,029
	3	9	11,97	0,872	2,220
	4	9	23,19	1,486	3,153
	5	9	–0,007	0,017	0,025
	6	9	5,55	0,191	1,062
	7	9	10,21	0,525	1,664

Annex B
(informative)

International inter-laboratory test programme to compare the TXRF method with the GF-AAS and ICP-MS methods

B.1 Introduction

An international inter-laboratory test programme was carried out using a GF-AAS method and an ICP-MS method in order to compare the results with those obtained with the TXRF method. Eleven laboratories in Japan, Europe and the USA participated in the programme. Two laboratories determined Fe and Ni by both the GF-AAS or ICP-MS method and the TXRF method, while the other nine laboratories used only the GF-AAS method or the ICP-MS method.

Testing was carried out in the same manner as described in Clause A.1. Eleven sets of measurements were obtained from eleven laboratories.

Statistical analysis of the measurement results was performed in accordance with ISO 5725-2.

B.2 Test specimens

The test specimens were the same as those shown in Table A.1.

B.3 Procedure for collection and determination of contamination elements

The Fe and Ni on the test specimens were collected in accordance with Clause 10 and determined by GF-AAS or ICP-MS using the laboratory's own procedure.

B.4 Statistical analysis

B.4.1 General

After the confirmation of measurement stability, absence of additional accidental contamination during measurements and uniformity of the specimen lots, the repeatability and the reproducibility were calculated in accordance with ISO 5725-2.

B.4.2 Statistical tests for outliers

Mandel's, Cochran's and Grubb's tests specified in ISO 5725-2 were applied to all reported measurement data at the 99 % confidence level. Table B.1 shows the number of specimens remaining after excluding outliers.

Table B.1 — Number of specimens remaining after exclusion of outliers

Laboratory	Number of specimens after exclusion of outliers													
	Fe							Ni						
	Level							Level						
	1	2	3	4	5	6	7	1	2	3	4	5	6	7
10	4	4	4	4	4	4	4	4	4	4	4	4	4	4
11	4	4	4	4	4	4	4	4	4	4	4	4	4	4
12	4	4	4	4	4	4	4	4	4	4	4	4	4	4
13	4	4	4	4	4	4	4	4	4	4	4	4	4	4
14	4	3	4	4	2	4	4	4	3	4	4	4	4	4
15	0	4	4	4	4	4	4	4	4	4	4	4	4	4
16	2	2	2	2	2	2	2	2	2	2	2	2	0	2
17	4	3	3	4	2	4	4	4	3	4	4	4	4	4
18	2	0	2	0	2	2	0	2	0	2	0	2	2	0
19	4	4	4	4	4	3	4	4	4	4	4	4	3	4
20	4	4	4	4	4	4	4	4	4	4	4	4	4	4

NOTE 1 Data from blank specimens of levels 1, 2 and 5 were excluded if the Fe or Ni density was above 1×10^{10} atoms/cm^2.

NOTE 2 Laboratories 16 and 18 analysed only two of the four specimens at each level. The other two specimens were analysed by the TXRF method.

B.4.3 Calculation of repeatability and reproducibility

All data after the exclusion of outliers were processed in accordance with ISO 5725-2 in order to obtain the repeatability and the reproducibility of the GF-AAS method and the ICP-MS method.

B.5 Results of statistical analysis

When calculating statistical data, the level 1 measurements from each laboratory were used as blank data for the level 2 and level 5 measurements from that laboratory. Level 2 and level 5 were also used as blank data for levels 3 and 4 and levels 6 and 7, respectively, for each laboratory.

The results of the statistical analysis of the reported measurement data are shown in Table B.2. The general mean values for levels 3, 4, 6 and 7 obtained by the GF-AAS method or the ICP-MS method were higher than those obtained by the TXRF method.

It should be noted that the repeatability and the reproducibility data include errors due to any unavoidable inhomogeneity of the specimens.

Table B.2 — Repeatability and reproducibility of reported measurement data after exclusion of outliers

Level		**Number of laboratories** p	**General mean** m $\times 10^{10}$ atoms/cm^2	**Repeatability** s_r $\times 10^{10}$ atoms/cm^2	**Reproducibility** s_R $\times 10^{10}$ atoms/cm^2
Fe	1	10	0,12	0,145	0,165
	2	10	–0,014	0,182	0,217
	3	11	13,66	0,481	2,140
	4	10	31,38	1,522	3,486
	5	11	0,036	0,130	0,205
	6	11	6,78	0,523	1,192
	7	10	12,87	0,370	1,903
Ni	1	11	0,083	0,073	0,102
	2	10	–0,027	0,035	0,068
	3	11	12,80	0,590	1,940
	4	10	23,55	1,034	2,278
	5	11	–0,020	0,091	0,111
	6	11	6,059	0,338	0,808
	7	10	12,21	0,476	1,974

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