
**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**

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*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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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*.

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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/cm² to 1×10^{14} atoms/cm², also a vapour-phase decomposition (VPD) method for atomic surface densities from 5×10^8 atoms/cm² to 5×10^{12} atoms/cm².

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/cm², 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.

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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

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/cm² to 5×10^{11} atoms/cm².

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 µg/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 µg/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 µg/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 µg/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 µg/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 µg/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.

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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. 7,3 mol/l of hydrofluoric acid and ca. 0,7 mol/l of hydrogen peroxide.

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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.