

SEMI M33-0998 (Withdrawn 1107)

TEST METHOD FOR THE DETERMINATION OF RESIDUAL SURFACE CONTAMINATION ON SILICON WAFERS BY MEANS OF TOTAL REFLECTION X-RAY FLUORESCENCE SPECTROSCOPY (TXRF)

This standard was technically approved by the global Silicon Wafer Committee. This edition was approved for publication by the global Audits and Reviews Subcommittee on September 5, 2007. It was available at www.semi.org in October 2007 and on CD-ROM in November 2007. Originally published September 1998.

NOTICE: This document was balloted and approved for withdrawal in 2007.

1 Purpose

1.1 The test provides the analytical procedure to determine the trace level of contaminating elements of an atomic number higher than 15 on polished or epitaxial silicon wafer surfaces in native or thermally grown or tetraethylorthosilicate (TEOS) oxide or in residues of microdroplets of process chemicals or media as analyzed with TXRF on silicon wafer surfaces as described in ¶ 15.1 and ¶ 15.2.

2 Scope

2.1 This document specifies a VPD-TXRF (Vapor Phase Decomposition Total Reflection X-Ray Fluorescence Spectroscopy) method to analyze the elemental composition and areal density of impurities, that include cations and anions with atomic numbers between 16 (S) and 92 (U) independent of their chemical state, with the exception of the X-ray source material, on polished or epitaxial silicon wafer surfaces in native or thermally grown oxide or in residues of microdroplets of process chemicals or media as analyzed with TXRF on silicon wafer surfaces.

2.2 This test is especially useful for analyzing metallic elements such as K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, (Mo), Pd, Ag, Sn, Sb, Ta, (W), Pt, (Au), Hg, and Pb and non-metallic elements such as S, Cl, As, Br, and I through their characteristic K and L lines. (Elements in brackets are usual X-ray sources.) For limitations in the nature of analytes refer to the note in ¶ 14.7.

2.3 This test method can be used to analyze areal surface contamination that can be collected in a microdroplet during the specified VPD preparation and the collection of the digested surface contamination in the range of 5×10^8 through 5×10^{12} atoms/cm².

2.4 Theoretically, the detection limit (LOD) of each analyte depends upon its atomic number. As defined by DIN 32645 "Limit of detection, determination and quantification" the LOD of TXRF is also depending upon many parameters, such as:

- excitation energy,
- intensity of incident X-ray,
- instrumental background,
- crystallographic interferences, such as Bragg diffraction conditions,
- impurities in the beam path,
- contamination of the blank scanning solution (see ¶ 4.5),
- contamination level in the analytical ambient,
- surface microroughness of wafer at the microdroplet (see ¶ 6.7), and
- integration time.

2.5 Concerning the surface conditions to be analyzed, the VPD-TXRF method is invasive. Nevertheless, the TXRF analysis of the microdroplet residue can be repeated many times provided that the prepared specimen is stored in a clean environment. The substrate and/or surrogate wafers can be recycled for monitoring purposes.

2.6 The user of this test method must assure that the metrology equipment is under control by the procedures commonly utilized in the performing laboratory. In the absence of established control procedures the use of 4.11.2 EN-ISO 9001 is recommended.

NOTICE SAFETY PRECAUTIONS — This standard does not purport to address the safety concerns, associated with its use. It is the responsibility of the user of this standard to establish and maintain appropriate safety and health practices and comply with the local regulatory ordinance. X-ray irradiation and handling of HNO_3 , HF and H_2O_2 are dangerous. Operators must comply with X-ray safety regulations and be trained to wear protective garments and glasses when handling HNO_3 , HF and H_2O_2 . These chemicals should be handled in a ventilated area (under exhaust.)

3 Referenced Standards and Documents

3.1 SEMI Standards

SEMI C7.3 — Standard for Hydrofluoric Acid, Grade 2

SEMI C7.5 — Standard for Hydrogen Peroxide, Grade 2

SEMI C7.6 — Standard for Nitric Acid, Grade 2

SEMI C10.1 — Guide for Determination of Method Detection Limits for Trace Metal Analysis by Plasma Spectroscopy

SEMI E45 — Test Method for the Determination of Inorganic Contamination from Minienvironments

SEMI M1 — Specifications for Polished Monocrystalline Silicon Wafers

SEMI M20 — Specification for Establishing a Wafer Coordinate System

3.2 ASTM Specifications¹

ASTM D5127 — Standard Guide for Electronic Grade Water (Type E-1)

ASTM E691 — Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

ASTM F1526 — Test Method for Surface Metals/TXRF

3.3 DIN Specifications²

DIN-ISO 5725 — Precision of Test Methods, Evaluation of Round-robins

DIN 12650 Part 6 — Gravimetric Test for Piston Operated Volumetric Apparatus

DIN 12650 Part 6 (Apr. 1983) — Gravimetric Test for Piston Operated Volumetric Apparatus

DIN 32645 — Limit of Detection and of Quantification

3.4 ISO Specifications³

EN-ISO-DIN 9001 — Quality Systems; Quality Assurance

3.5 Other Specification⁴

U.S. Federal Standard 209 — Airborne Particulate Cleanliness Classes in Cleanrooms and Clean Zones

4 Terminology

4.1 *anglescan* — a measurement of the emitted fluorescence signal as a function of the glancing angle of incident X-ray beam.

4.2 *areal density* — amount of impurities in a unit area of native or thermally grown silicon oxide as converted from the detected amount of analytes into the whole analyzed (i.e., scanned surface area).

4.3 *as-polished wafer* — mirror-finished wafer planarized by chemi-mechanical polishing.

1 American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585; Fax: 610.832.9555; <http://www.astm.org>

2 Deutsches Institut für Normung e.V., Available from Beuth Verlag GmbH, Burggrafenstrasse 4-10, D-10787 Berlin, Germany; <http://www.din.de>

3 International Organization for Standardization, ISO Central Secretariat, 1 rue de Varembe, Case postale 56, CH-1211 Geneva 20, Switzerland. Telephone: 41.22.749.01.11; Fax: 41.22.733.34.30; <http://www.iso.ch>

4 Available from Standardization Documents Order Desk, Bldg. 4, Section D, 700 Robbins Avenue, Philadelphia, PA 19111-5094, Attn: NPODS

4.4 *azimuthal position* — orientation around the z-crystal/ingot axis as specified in SEMI M20.

4.5 *contamination collection* — microanalytical method to collect the VPD decomposition products from the silicon surface by rolling a scanning microdroplet on the hydrophobic silicon wafer surface after VPD preparation as originally described in ¶¶ 15.2, 15.4, and 15.5 (also see ¶ 8.3 of this document).

4.6 *critical angle* — the incident X-ray glancing angle below which total reflection of the incident X-ray occurs. At the critical angle the X-ray reflection equals 0.5.

4.7 *detection spot area* — the surface area where above the fluorescence counts are integrated.

4.8 *epitaxial wafer* — as-polished wafer covered with a layer of monocrystalline silicon deposited from a heterogeneous phase.

4.9 *glancing angle* — incidence angle of X-ray excitation.

4.10 *hydrophobic surface* — contact angle of wafer > 60° (e.g., virgin epitaxial or HF- or HMDS (hexamethyldisilazane) -treated surface as described in ¶ 15.3).

4.11 *impurities* — elements in/on the specimen other than silicon or elements in ultra pure process media as listed in ¶ 2.2.

4.12 *native oxide* — compound of silicon, oxygen, and water on as-polished or epitaxial wafer, grown in air or in cleaning solutions.

4.13 *recovery rate* — the ratio of analytes found after the first VPD and contamination collection procedure to the sum of the analytes found after two or more repeated scanning with unused scanning droplet of unchanged chemical composition.

NOTE 1: Recent efforts of the Statistical Task Force of the SEMI Chemicals and Gases Committee may result in a new definition (see ¶ 14.2 of this document).

4.14 *spurious peaks* — peaks that are detected but not originated from impurities of the silicon wafer (c.f., 6.1).

4.15 *thermally grown oxide* — SiO₂ up to 1000 nm thickness deposited or grown in thermal processing in oxygen containing atmosphere.

4.16 *vapor phase decomposition (VPD)* — vapor phase decomposition of silicon oxides using HF vapor at room temperature as a surface preparation method for microanalysis, as originally described in ¶¶ 15.2, 15.4, or 15.5 (also see ¶ 5.1 and § 11 of this document).

5 Summary of Method

5.1 The native or thermally grown oxide layer of the silicon surface is converted with HF vapor into fluid droplets that contain the impurities of the oxide layer. With a scanning droplet the fluid reaction products are collected in one microdroplet. That microdroplet is dried on the wafer under controlled conditions and analyzed with TXRF.

5.2 Similarly, a microdroplet of process chemicals or media can be dried on hydrophobic polished or epitaxial silicon wafer under controlled conditions and analyzed with TXRF.

5.3 Preferably, monochromatic and collimated X-rays irradiate a planarized and chemi-mechanically polished, monocrystalline silicon wafer surface. The X-rays impinge the surface at a glancing angle that is below the angle for total reflection of the X-rays, preferably, at an incident angle 70% of the angle of total reflection [1.3 mrad (or 0.07°) for Mo target and 2.0 mrad (or 0.11°) for W target].

5.4 The evanescent waves excite the fluorescence energy levels of the surface atoms, which then emit fluorescence X-rays characteristic of their atomic number. The emitted X-rays are detected by a solid state detector that is an energy dispersive spectrometer. In the range of specified areal density (compare with ¶ 2.3 of this document) the integrated count rate (cps) is linearly proportional to the elemental areal density.

5.5 For quantification, the linear regression must be established (c.f., ¶ 15.6) or a linear proportionality is anticipated between the cps data that are measured above the certified reference microdroplet(s) and the cps data that are measured above the microdroplet of the unknown analytes without changing the anglescan conditions, according to ¶¶ 9.1, 13.6, and 15.7.

6 Interferences

6.1 The known interferences in X-ray fluorescence spectroscopy also affect TXRF. Thus, overlapping fluorescence lines, escape peak, energy gain drift, X-ray source stability, beam path background contamination must be evaluated according to ¶ 15.7 of this document.

6.2 Baseline corrections due to varying background contamination must be controlled by the rules of statistical analysis (e.g., as described in ¶ 15.8 of this document).

6.3 Under the specified conditions, no corrections are required for secondary fluorescence or for oscillations or for matrix absorption as described in ¶ 15.9–¶ 15.11 of this document.

6.4 Accuracy of the standard reference specimen and positioning accuracy and precision of the detector define the bias in the assigned areal density.

6.5 Mechanical vibration may degrade the detector resolution and it can also decrease the selectivity.

6.6 Multielement contamination degrades the LOD compared with monoelement contamination.

6.7 Increased surface microroughness and/or high-total signal count rates result in high deadtime and can lead to non-linearity of detected fluorescence signal versus areal density (i.e., to degradation of LOD).

6.8 Under optical conditions satisfying the Bragg reflections the background noise depends upon the azimuthal orientation of the sample. Before quantification, a determination of the azimuthal angular range, that shows minimum Bragg reflection background, is recommended. Otherwise the LOD may degrade due to high background and spurious peaks.

6.9 During handling and measurement particles or volatile contamination (e.g., NH_3) from the analytical environment must be controlled and avoided.

6.10 During measurement Ar must be excluded from the analytical ambient (e.g., by evacuating the chamber or flushing it with He).

6.11 Curve smoothing and evaluation algorithms with controlled Fourier parameters or Digital Filtering are preferred to direct count rate evaluation because these algorithms provide a higher level of statistical confidence than a software that directly quantifies cps as described in ¶ 15.12 of this document.

6.12 Recovery rates as defined in ¶ 4.13 of this document depend upon the distribution of the analytes between the scanning solution (solubility) and silicon surface (adsorption and plating). Therefore, recovery rates depend on the:

- applied scanning solution (¶ 4.5, ¶ 8.3),
- chemical nature of the different analytes/elements, and
- physical and physicochemical state of the silicon surface.

6.13 Automated contamination collection procedure (scanning) increases the wafer-to-wafer reproducibility of the described method as reported in ¶ 15.13 of this document.

7 Apparatus

7.1 The VPD treatment and contamination collection particularly, but also the handling and measurement of the specimen wafer is to be carried out in a specified and controlled ambient (e.g., Cl. 10 (U.S. Federal Standard 209)).

7.2 TXRF system equipped with:

- an X-ray source,
- a monochromator (preferable),
- a sample stage capable of manipulating in the x-, y-, and z-direction,
- automated test specimen handling,
- an energy-dispersive spectrometer X-ray detector,
- software sub-routine for glancing angle calibration,