



Standard Test Method for Measuring Surface Metal Contamination on Silicon Wafers by Total Reflection X-Ray Fluorescence Spectroscopy¹

This standard is issued under the fixed designation F 1526; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the quantitative determination of elemental areal density on the surface of polished single crystal silicon substrates using total reflection X-ray fluorescence spectroscopy (TXRF²) with a monochromatic X-ray source.³

1.2 This test method can be used for both *n*-type and *p*-type silicon.

1.3 This test method can be used to detect surface elemental contamination that is within the analyte depth of approximately 5 nm for highly mirror-polished silicon wafers. The analytic depth increases with surface roughness.⁴

1.4 This test method is especially useful for determining the surface elemental areal densities in the native oxide or in chemically grown oxide of polished silicon wafers after cleaning.

1.5 This test method is useful for elemental areal densities between 10^9 and 10^{15} atoms/cm² within the measurement area. See Annex A1 for a discussion of the relationship between repeatability and detection limit.

1.6 This test method is useful for detecting elements with atomic number between 16 (S) and 92 (U), depending upon the X-ray source provided in the instrument. This test is especially useful for detecting the following metals or elements: potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, molybdenum, palladium, silver, tin, tantalum, tungsten, platinum, gold, mercury, and lead.

1.7 The detection limit depends upon atomic number, excitation energy, photon flux of excitation X-rays, instrumental background, integration time, and blank value. For constant instrumental parameters, the interference-free detection limits

vary over two orders of magnitude as a function of atomic number of the element.

1.8 This test method is nondestructive.

1.9 This test method is complementary to a variety of other test methods:

1.9.1 Electron spectroscopy for chemical analysis that can detect elemental surface areal densities down to the order of 10^{13} atoms/cm².

1.9.2 Auger electron spectroscopy that can detect elemental surface areal densities down to the order of 10^2 atoms/cm².

1.9.3 Nitrogen-beam Rutherford backscattering spectrometry that can detect down to 10^{10} atoms/cm² for some elements but cannot mass resolve heavy elements of nearby atomic number.

1.9.4 Secondary ion mass spectrometry that can detect low-atomic-number elemental areal densities in the range of 10^8 to 10^{12} atoms/cm² but cannot provide adequate detection limits for transition metals with atomic number between 22 titanium and 30 zinc. This method is destructive.

1.9.5 Vapor phase decomposition (VPD) of surface metals followed by atomic absorption spectroscopy (AAS), where the metal detection limits are from 10^8 to 10^{11} atoms/cm², but there is no spatial information available and the analysis time is longer than TXRF. This method is destructive.

1.10 This test method uses X-radiation; it is absolutely necessary to avoid personal exposure to X-rays. It is especially important to keep hands or fingers out of the path of the X rays and to protect the eyes from scattered secondary radiation. The use of commercial film badge or dosimeter service is recommended, together with periodic checks of the radiation level at the hand and body positions with a Geiger-Muller counter calibrated with a standard nuclear source. The present maximum permissible dose for total body exposure of an individual to external X-radiation of quantum energy less than 3 MeV over an indefinite period is 1.25 R (3.22×10^{-4} C/kg) per calendar quarter (equivalent to 0.6 mR/h (1.5×10^{-7} C/kg-h)) as established in the Code of Federal Regulations, Title 10, Part 20. The present maximum permissible dose of hand and forearm exposure under the same conditions is 18.75 R (4.85×10^{-3} C/kg) per calendar quarter (equivalent to 9.3 mR/h (2.4×10^{-6} C/kg-h)). Besides the above stated regulations, various other government and regulatory organizations have their own safety requirements. It is the responsibility of the user to make sure that the equipment and the conditions

¹ This test method is under the jurisdiction of ASTM Committee F01 on Electronics and is the direct responsibility of Subcommittee F01.06 on Silicon Materials and Process Control.

Current edition approved Sept. 15, 1995. Published November 1995. Originally published as F 1526 – 94. Last previous edition F 1526 – 94a.

² There are several acronyms in use: TXRF, TRFA, and TRXRF; however, TXRF is the most common in the technical literature.

³ There are some non-monochromatic TXRF instruments that are no longer commercially available and that do not provide the detection limits described herein.

⁴ The extreme case of roughness on the backside of wafers is addressed by Hockett, R. S., "TXRF Measurement of Substrate Backside Contamination," Cleaning Technology in Semiconductor Device Manufacturing, ECS Proceedings, Vol 92-12, The Electrochemical Society, Inc., Pennington, NJ, 1992, p. 350.

under which it is used meet these regulations (see 1.11).

1.11 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

E 122 Practice for Choice of Sample Size to Estimate a Measure of Quality of a Lot or Process⁵

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials⁶

2.2 Federal Standard:

CFR Title 10, Part 20⁷

3. Terminology

3.1 Most terms used in this test method are defined in Terminology E 135.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *anglescan*—a measurement of the emitted fluorescence signal as a function of glancing angle.

3.2.2 *critical angle*—the incident X-ray glancing angle below which total external reflection of the incident X-ray occurs.

4. Summary of Test Method

4.1 Fig. 1 shows a block diagram of the technique. Monochromatic X rays from an X-ray source impinge the surface of a polished silicon substrate at a glancing angle that is below the angle for total external reflection of the X rays. The evanescent wave of the X rays penetrates the polished silicon surface with an exponential decay of intensity versus depth dependent upon the total electron density of the native oxide and the silicon

substrate. One exponential decay length is approximately 5 nm for silicon of all resistivity.

4.2 The evanescent wave excites the fluorescence energy levels of the surface atoms which then emit fluorescence X-rays characteristic of their atomic number. Emitted fluorescence X-rays are detected by a lithium-drifted silicon detector, or other solid state detector, which is an energy dispersive spectrometer. Experience indicates that for measurement of samples with high levels ($>10^{11}$ atoms/cm²) of specific elements that have been measured with other methods, such as those listed in 1.9, the integrated counts per second under the fluorescence peaks are linearly proportional to the elemental areal density.

4.3 Reproducible, rapid analysis can be accomplished using a calibration specimen, supplied by the TXRF instrument manufacturer or developed by another company, with at least one known elemental areal density in the measurement area. This calibration specimen is analyzed by the TXRF instrument to provide a measured number of integrated fluorescence counts per second corresponding to the known elemental areal density. Then one or more test specimens are analyzed under the same instrumental conditions. The integrated fluorescence counts per second for the elements detected on the test specimen are quantified using relative sensitivity factors (RSFs) with respect to the calibration element count rate per known areal density, where the RSFs are contained within the instrument software. The lack of true standards precludes determination of the accuracy of this test method.

5. Significance and Use

5.1 TXRF can measure the elemental, particularly metal, areal densities on polished silicon wafer product.

5.2 The TXRF measurement facilitates the production of silicon wafers with controlled upper limits on metal areal densities.

5.3 This test method can be used for monitoring a mirror-polished wafer cleaning process, research and development, and materials acceptance purposes.

6. Interferences

6.1 The interferences in conventional X-ray fluorescence spectroscopy are common to TXRF also. These include, but are not limited to: overlap of fluorescence lines, escape peak and sum peak overlap, energy gain calibration drift, X-ray source stability, and instrumental background peaks. However, no X-ray fluorescence corrections for secondary fluorescence or for matrix absorption are required for TXRF. Interferences common to software procedures and calculations can be evaluated by comparing data sets; see Annex A1.

6.2 In addition to conventional interferences, there are interferences that are unique to TXRF as follows:

6.2.1 If the glancing angle calibration is not reproducible, variability is introduced to the measurement,

6.2.2 If the glancing angle calibration is inaccurate, bias is introduced to the measurement,

6.2.3 If the anglescan of the known elemental impurity on the calibration specimen is different from the elemental impurity anglescan on the test specimen, this may introduce a bias to the quantification. An example can be the measurement of

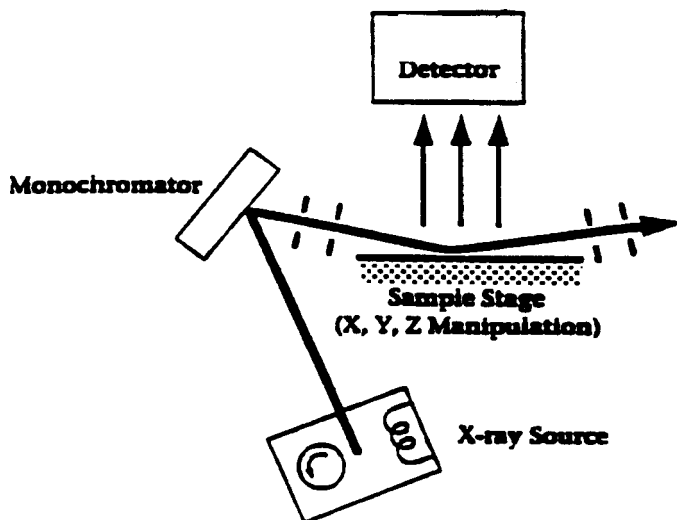


FIG. 1 Block Diagram of the TXRF Technique

⁵ Annual Book of ASTM Standards, Vol 14.02.

⁶ Annual Book of ASTM Standards, Vol 03.05.

⁷ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

particulate metal contamination on a test specimen while using a calibration specimen which has the calibration metal localized within the native oxide,

6.2.4 Mechanical vibration may degrade the detector energy resolution, and this may degrade detection limits,

6.2.5 If the specimen is not chem-mechanically polished, there will be a loss in detection capability, a bias in quantification, and an increase in variability of the measurement. There is some possibility that the surface roughness and waviness differences from different cleaning processes may cause these interferences also. The semiquantitative effect of surface roughness upon the TXRF measurement is under study.

6.2.6 Bias in the assigned elemental areal density of the calibration specimen can introduce bias into the TXRF measured areal densities,

6.2.7 Surface contamination introduced during handling of the test specimens or during the measurement itself will introduce a bias to the measurement, if this surface contamination contains the element(s) to be measured,

6.2.8 Bias in the RSF of a fluorescence line can introduce bias to the measurement,

6.2.9 Nonlinearity of detected fluorescence signal versus impurity areal density may occur due to high deadtime of some detectors under the condition of high-total signal count rates, and

6.2.10 Fluorescence curve smoothing may affect the quantification accuracy.

6.2.11 Instrumental peaks may be generated by the incident X-ray beam diffracting from the silicon crystal and the diffracted beam entering the detector to excite metals in the detector window or detector housing. This effect can be tested for by appropriate experiments.⁸

7. Apparatus

7.1 *TXRF Instrument*, equipped with a monochromatic X-ray source, test specimen handling equipment, a method for glancing angle calibration, an energy-dispersive spectrometer X-ray detector, software for background subtraction, peak integration, analysis and RSFs, and an analysis ambient without argon (for example, vacuum of 10^{-2} torr, or helium gas). The methods for glancing angle calibration are presently proprietary for each TXRF instrument manufacturer. A TXRF manufacturer may include a subtraction routine for escape peaks and these signals may already be removed.

7.2 *Reference Wafer*—The suitability of the apparatus shall be determined with the use of a reference wafer and its associated data set in accordance with the procedures of Annex A2, or by performance of a statistically-based instrument repeatability study to ascertain whether the equipment is operating within the manufacturer's stated specification for repeatability.

7.3 *Class 100 Air Environment*—The area for sample transfer to the instrument measurement stage must be enclosed in this.

⁸ Yakushiji, K., Ohkawa, S., Yoshinga, A., and Harada, J., "Origins of Spurious Peaks of Total Reflection X-Ray Fluorescence Analysis of Si Wafers Excited by Monochromatic X-Ray Beam W1-beta," Japanese Journal of Applied Physics, Vol 33, 1994, pp. 1130—1135.

8. Sampling

8.1 A sampling procedure must be used to evaluate the characteristics of a group of silicon wafers. No general sampling procedure is included as part of this test method, because the most suitable sampling plan will vary considerably depending upon individual conditions. For referee purposes, a sampling plan shall be agreed upon before conducting the test. See Practice E 122 for suggested choices of sampling plans.

9. Specimen Requirements

9.1 Test specimens must be chem-mechanical polished on the side used for analysis.

10. Test Specimen Measurement

10.1 Load the test specimen into the TXRF instrument in a contamination free environment of Class 100 or better.

10.2 Measure the TXRF spectrum for the test specimen.

10.3 Calculate the net integrated counts/second for detected elemental peaks.

10.4 Using the calibration wafer data for the calibration element and the RSFs for the other elements, calculate the elemental areal densities for each detected element on the test specimen according to Eq 1.

$$D_{u,m} = (1/F_{s,m}) \times (CPS_{u,m}) \times (CPS_s)^{-1} \times (A_s) \quad (1)$$

where:

$D_{su,m}$ = the areal density in atoms/cm² of element "m" on the test specimen "u",

$F_{s,m}$ = the RSF of element "m" with respect to the calibration element "s",

$CPS_{u,m}$ = the integrated counts/second of element "m" detected on test specimen "u",

CPS_s = the integrated counts/second of the calibration element on the calibration standard, and

A_s = the assigned areal density in atoms/cm² of the calibration element.

11. Calibration Standard

11.1 The calibration standard and the method of its preparation must be agreed upon between the parties.

NOTE 1—Several methods for preparing calibration standards are in practice.⁹

The present state-of-the-art calibration standard is a chem-mechanical polished silicon substrate with a surface metal areal density of between 1 by 10^{12} and 1 by 10^{14} atoms/cm² located in the analysis area. The k -alpha fluorescence signal from the calibration standard metal is free of interferences, that is, escape peaks, sum peaks, and fluorescence peaks from other contamination, and free from external contamination sources. The preferred element should not be easily added as a contaminated element (for example, iron) or diffuse away from the analyte depth over time (for example, gold or copper). The preferred element is nickel or vanadium. Calibration can also be done using a set of wafers with different known areal densities of a particular element.

The calibration standard should have been measured by an appropriate analytical method to determine the metal areal density of the calibration

⁹ Hockett, R. S., "TXRF Reference Standards: A Discussion," Contamination Control and Defect Reduction in Semiconductor Manufacturing III, Vol 94-9, edited by Dennis N. Schmidt, The Electrochemical Society, Pennington, NJ, 1994, pp. 323-334.