Designation: F 1526 – 95 (Reapproved 2000)

Standard Test Method for Measuring Surface Metal Contamination on Silicon Wafers by Total Reflection X-Ray Fluorescence Spectroscopy [1]

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 (TXRF[2]) 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/cm^2 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/cm^2.

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

1.9.3 Nitrogen-beam Rutherford backscattering spectrometry that can detect down to 10^{10} atoms/cm^2 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/cm^2 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/cm^2, 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.

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[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 Process [5]

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[6]

2.2 *Federal Standard:*

CFR Title 10, Part 20 [7]

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/cm^2) 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

[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.

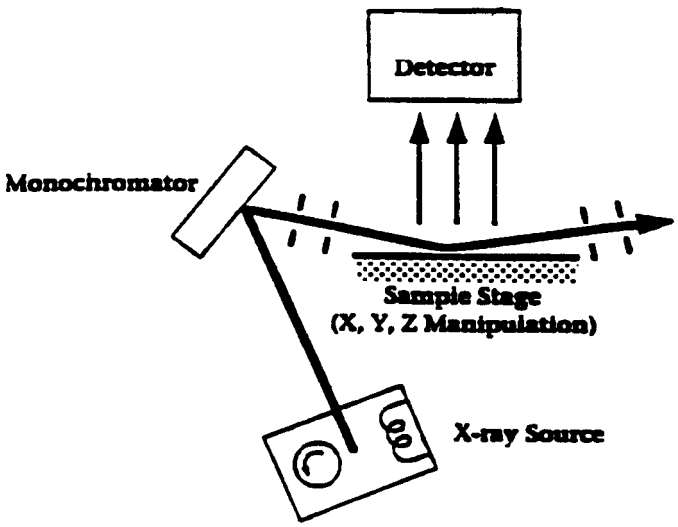

FIG. 1 Block Diagram of the TXRF Technique