



Standard Test Method for Measuring Surface Sodium, Aluminum, Potassium, and Iron on Silicon and EPI Substrates by Secondary Ion Mass Spectrometry¹

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1. Scope

1.1 This test method covers the determination of total sodium, aluminum, potassium, and iron on the surface of mirror-polished single crystal silicon and silicon epi substrates using secondary ion mass spectrometry (SIMS). This test method measures the total amount of each metal, because this test method is independent of the metal's chemistry or electrical activity.

1.2 This test method can be used for silicon with all dopant species and dopant concentrations.

1.3 This test method is especially designed to be used for surface metal contamination that is located within approximately 5 nm of the surface of the wafer.

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

1.5 This test method is useful for sodium, aluminum, potassium, and iron areal densities between 10^9 and 10^{14} atoms/cm². The limit of detection is determined by either the BLANK value or by count rate limitations, and may vary with instrumentation.

1.6 This test method is complementary to:

1.6.1 Total reflection X-ray fluorescence (TXRF), that can detect higher atomic number Z, surface metals such as iron, but does not have useful ($<10^{11}$ atoms/cm²) detection limits for sodium, potassium, and aluminum on silicon.

1.6.2 Electron spectroscopy for chemical analysis and Auger electron spectroscopy that can detect metal surface areal densities down to the order of 10^{12} to 10^{13} atoms/cm².

1.6.3 Vapor phase decomposition (VPD) of surface metals followed by atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectrometry (ICP-MS) of the VPD residue, where the metal detection limits are 10^8 to 10^{10} atoms/cm². There is no spatial information available and the VPD preconcentration of metals is dependent upon the chemistry of each metal.

1.7 *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 for a Lot or Process²

E 673 Terminology Relating to Surface Analysis³

3. Terminology

3.1 All terms in this test method are in conformance with those given in Terminology E 673.

4. Summary of Test Method

4.1 Specimens of mirror-polished single crystal silicon are loaded into a sample holder. The holder is transferred into the analysis chamber of the SIMS instrument.

4.2 A primary ion beam, typically O₂⁺, is used to bombard each specimen with a sputter rate less than 0.015 nm/s (0.9 nm/min).

4.3 The area of analysis may be different for different instruments and may range from 100 μm × 100 μm to 1 mm × 1 mm.

4.4 Depending upon instrumentation, a molecular oxygen jet or leak may be focused on the analysis area.

4.5 The positive secondary ions ²³Na, ²⁷Al, ³⁹K, and ⁵⁴Fe are mass analyzed by a mass spectrometer, and detected by an electron multiplier (EM) or equivalent high-sensitivity ion detector as a function of time until the signals reach background levels or 1 % of the initial signal rates of each element. The instrumentation must be able to discriminate the elemental ion signals from molecular interferences.

4.6 A BLANK silicon sample is used to evaluate whether the lower limit of detection arises from molecular ion interferences, elemental instrumental backgrounds, or count rate limitations. The matrix positive secondary ion count rate for silicon (²⁸Si, ²⁹Si, or ³⁰Si) is measured by a faraday cup (FC) or appropriate detector during, or at the end of, the profile. If

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

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² Annual Book of ASTM Standards, Vol 14.02.

³ Annual Book of ASTM Standards, Vol 03.06.

multiple detectors are used during the test, the relative sensitivities of the detectors are determined by measuring standard ion signals (either the same positive secondary ion count rate or ion count rates of known relative intensity such as natural $^{28}\text{Si}/^{30}\text{Si}$) on each detector.

4.7 The net integrated ^{23}Na , ^{27}Al , ^{39}K , and ^{54}Fe signals are converted to quantitative areal densities using the detector efficiency ratios (if multiple detectors are used) and relative sensitivity factors (RSFs) measured from reference materials.

NOTE 1—The discrimination of elemental ions from molecular ions is particularly important for the $^{27}\text{Al}^+$ signal that has a significant interference below about 10^{11} to 10^{12} atoms/cm² from ubiquitous C_2H_3^+ molecular ions that may arise from clean room air or from plastic cassette containers. The relative importance of the organic interference is dependent upon the surface organics of the test wafer. Another significant interference occurs from ubiquitous BO^+ when the aluminum is in the range of 10^9 to 10^{10} atoms/cm², since surface boron at the 10^{12} atoms/cm² range is common for all wafers, both *n*-type as well as *p*-type.⁴ If the surface contains high levels of sodium, there may be a NaO^+ molecular interference for $^{39}\text{K}^+$. In principle, $^{11}\text{B}^{12}\text{C}^+$ and $^{11}\text{B}^{28}\text{Si}^+$ can be a molecular interferences for $^{23}\text{Na}^+$ and $^{39}\text{K}^+$ respectively. The $^{54}\text{Fe}^{+1}$ signal can have interferences from $^{27}\text{Al}_2^{+1}$ or $^{54}\text{Cr}^{+1}$. Discrimination of molecular ion interferences can be achieved using magnetic mass spectrometers operated under high mass resolution or in some cases using quadrupole mass spectrometers via energy filters.⁵

5. Significance and Use

5.1 SIMS can measure on polished silicon wafer product the following:

- (1) the sodium and potassium areal densities that can affect voltage flatband shifts in integrated circuits, and,
- (2) the aluminum areal density that can affect the thermal oxide growth rate.
- (3) the iron areal density that can affect gate oxide integrity, minority carrier lifetime, and current leakage.

5.2 The SIMS measurement facilitates the production of silicon wafers with upper control limits on sodium, potassium, aluminum, and iron areal densities.

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

5.4 This test method can provide spatial information for these metal contaminants, including near-edge substrate contamination levels.

6. Interferences

6.1 Surface metal contamination of sodium, aluminum, potassium or iron introduced during handling of the test specimen or during the measurement itself will introduce a bias to the measurement. (Particulate room contamination containing these metals is easily distinguished from metal contamination by the shape of the SIMS profile that should have the log

of the signal drop linearly with time. A particulate contamination does not follow this shape under SIMS profile.)

6.2 Bias in the RSFs derived from reference materials can introduce bias into the SIMS measured areal densities.

6.3 Mass interferences can introduce bias if the instrument mass resolution, or subsequent detection scheme, is not sufficient to exclude the interference.

6.4 The SIMS sodium, aluminum, potassium, and iron instrumental backgrounds can limit the detection of low levels of surface metals.

6.5 The accuracy and precision of the measurement can be significantly degraded by analysis of specimens whose surfaces are not all at the same inclination with respect to the ion collection optics of the SIMS instrument. The specimen holder must be constructed and maintained such that after specimen(s) are loaded into the holder, the inclination of the surface of each specimen is constant from specimen to specimen.

6.6 The accuracy and precision of the measurement significantly degrade as the roughness of the specimen surface increases. This degradation can be avoided by using chem-mechanical polished surfaces.

6.7 If an oxygen leak is not used in conjunction with the measurement, there may be a bias due to the effect of different chemical native-oxide thicknesses upon ion yields. This effect has not been studied.

7. Apparatus

7.1 *SIMS Instrument*, equipped with a primary ion beam, preferably O_2^+ , a mass spectrometer with some method of discriminating molecular ion interferences from elemental ions of interest, an electron multiplier detector, or faraday cup detector, or similar detector system capable of measuring secondary ion count rates, or any combination thereof, and the ability to sputter the surface at less than 0.015 nm/s. An molecular oxygen jet may be used to stabilize the surface ion yield; the local oxygen gas flux to the specimen surface must be stable enough that the secondary ion yield does not vary during the analysis. The stability of the oxygen jet effect can be checked by monitoring a silicon matrix signal during a profile; and if the matrix signal is not monitored during a profile, the vacuum chamber pressure can be monitored for fluctuations in the oxygen gas pressure. The SIMS instrument should be adequately prepared and maintained so as to provide the lowest possible instrumental backgrounds.

7.2 *Test Specimen Holder*, reserved for the SIMS measurement. In some instruments the holder can support multiple 5 by 5-mm samples that are held face down against metal (tantalum) windows. In other instruments the holder can support one or more 15 by 15-mm samples by spring clips on the edge of the specimen or silver paste on the sample back surface. Some instruments can hold full silicon wafers. In all cases, the sample holder should be adequately prepared and maintained so as to provide the lowest possible contribution to instrumental backgrounds.

7.3 *Stylus Profliometer*, or equivalent device (for example, atomic force microscope) to measure SIMS crater depths. This is required to calibrate depth scales for concentration profiles of calibration standard samples. For routine depth scale calibration of test specimens, the instrument must be capable of

⁴ Mollenkopf, H., "Chemicals and Cleanroom Filtered Air Effects on Boron Contamination and Its Near Surface Detection in Silicon Wafers," *Extended Abstracts*, Vol 93-2, Abstract No. 170, The Electrochemical Society, Pennington, NJ, 1993, pp. 273-274.

⁵ Frost, M. R., "On the Use of Quadrupole SIMS for the Measurement of Surface Metallic Contamination," *Contamination Control and Defect Reduction in Semiconductor Manufacturing III, ECS Proceedings*, Vol 94-9, edited by D. N. Schmidt, The Electrochemical Society, Pennington, NJ, 1994, pp. 339-350.