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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Measuring Surface Sodium, Aluminum, Potassium, and Iron on Silicon and EPI Substrates by Secondary Ion Mass Spectrometry [1]

This standard is issued under the fixed designation F 1617; 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 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/cm^2. 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/cm^2) 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/cm^2 .

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/cm^2. 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 Process [2]

E 673 Terminology Relating to Surface Analysis [3]

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 O_2^+, 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 ^{23}Na, ^{27}Al, ^{39}K, and ^{54}Fe 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 (^{28}Si, ^{29}Si, or ^{30}Si) is measured by a faraday cup (FC) or appropriate detector during, or at the end of, the profile. If

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[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 $^{28}Si/^{30}Si$) 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 $^{27}Al^+$ signal that has a significant interference below about 10^{11} to 10^{12} atoms/cm^2 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/cm^2, since surface boron at the 10^{12} atoms/cm^2 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 $^{39}K^+$. In principle, $^{11}B\,^{12}C^+$ and $^{11}B\,^{28}Si^+$ can be a molecular interferences for $^{23}Na^+$ and ^{39}K respectively. The $^{54}Fe^{+1}$ signal can have interferences from $^{27}Al_2^{+1}$ or $^{54}Cr^{+1}$. 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) 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 Profilometer*, 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

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[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.

crater depth measurements of 10 nm with an accuracy and precision of 10 %. In the absence of such an instrument, a secondary depth calibration standard (such as a silicon wafer with a known impurity depth profile) must be prepared and can be used to measure the SIMS sputter rate during the measurement.

NOTE 2—The accurate measurement of sputter crater depths on the order of and below 10 nm is still an area of research, because the sputtered silicon is very reactive to oxygen in the air when removed from the SIMS chamber for crater depth measurement. For example, sputter craters expected to be only 1 nm in depth can actually be thicker than the original native oxide due to this rapid oxide growth on sputtered silicon, that is, one observes a bump on the surface where the erosion was, rather than a crater. If a reference sample is similar to the unknown in type, that is, intentional surface contamination rather than shallow ion implant, it may be possible to avoid the need for a direct shallow crater depth measurement on each sample.

8. Sampling

8.1 Since this procedure is destructive in nature, 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 Sample specimen surfaces must be flat and smooth (see 6.5 and 6.6).

9.2 Sample specimens must be cleaved or diced to fit within the sample specimen holder. Specimens need not be all the same size, but typical specimen sizes are approximately square with one side of dimension 5 to 15 mm.

9.3 Prepare a BLANK specimen with a level of surface metal below that expected to be detected by this test method, and which has surface organics of a level and type expected for the unknown specimens.

NOTE 3—If measurements are to be made on specimens taken soon after a cleaning process, the organics on the surface from clean room air and cassette carriers are very low and negligible. However, if the specimens are stored for one day or more, the level of organics may be significant for a molecular ion interference in the measurement [6]; this interference must be removed by the detection scheme.

10. Calibration

10.1 The calibration is by RSFs which are determined empirically from reference materials.

10.1.1 Reference materials may be either:

10.1.1.1 *Spin Coat Contaminated Samples*, calibrated by Vapor Phase Decomposition/Atomic Absorption Spectroscopy (VPD/AAS) or Vapor Phase Decomposition/Inductively-Coupled-Plasma Mass Spectrometry (VPD/ICP-MS) and shown by qualitative SIMS to be spatially uniform, since spatial non-uniformity can introduce variability or bias to the SIMS quantitative measurement. With a spin coat contaminated reference sample, it may be possible to avoid the need for the crater depth measurement and its bias/variability. For this reference sample the areal density D in (Eq 1) (see 12.1) is the elemental areal density determined by the VPD/AAs or VPD/ICP-MS, corrected for isotopic abundance since the SIMS measurement of SI_i is isotopic.

10.1.1.2 *Silicon Wafers*, dipped in an intentionally contaminated SC-1 ($NH_4OH:H_2O_2:H_2O$) bath where the calibration of the metal deposition is by VPD/AAS or VPD/ICP-MS and shown by qualitative SIMS, or by TXRF for iron, to be spatially uniform, since spatial non-uniformity can introduce variability or bias to the SIMS quantitative measurement. With an SC-1 dipped reference sample, it may be possible to avoid the need for the crater depth measurement and its bias/variability. For this reference sample the areal density D in (Eq 1) is the elemental areal density determined by the VPD/AAS or VPD/ICP-MS, corrected for isotopic abundance since the SIMS measurement of Si_i is isotopic.

10.1.1.3 *Ion Implants*, such as ^{23}Na, ^{27}Al, ^{39}K, and ^{56}Fe, (or ^{54}Fe) implanted into silicon and shown by qualitative SIMS, or by TXRF for iron to be spatially uniform, since spatial non-uniformity can introduce variability or bias to the SIMS quantitative measurement. It is necessary to demonstrate that RSFs obtained from these reference materials and the instrumentation and operation used for the measurement are consistent with RSFs from spin coated reference samples.[5] For this reference sample the areal density D in (Eq 1) is the implanted isotopic dose.

11. Procedure

11.1 *Specimen Loading* (Unknowns, Reference, BLANK) and SIMS Instrument Set-up:

11.1.1 Cleave or dice individual specimens (unknowns, reference, BLANK) to fit within the sample holder. The reference sample must contain ^{23}Na, ^{27}Al, ^{39}K, and ^{56}Fe (or ^{54}Fe) or there must be multiple reference samples, each with one or more of these elements. Do this preparation in such a way as to minimize contamination of the specimens with surface metals.

11.1.2 Load the specimen(s) into the SIMS sample holder.

11.1.3 Transfer the loaded holder into the SIMS instrument sample chamber.

11.1.4 Turn on the instrument in accordance with the manufacturer's instructions.

11.1.5 Set the appropriate analytical conditions including the method for molecular ion mass interference discrimination.

11.1.5.1 Select a primary ion current, primary beam raster size, and secondary spectrometer transmission, which will result in an appropriate sputter rate (less than 0.015 nm/s).

11.1.5.2 Select the secondary spectrometer conditions so that the maximum secondary ion-count rates result in dead time losses below 10 %.[7]

11.1.6 Confirm that analytical conditions are appropriate to the measurement goals by measurement of known reference

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[6] Muller, A. J., Sinclair, J. D., Psota-Kelty, L. A., and Krauttler, H. W., "Measurement of Airbourne Concentrations and Surface Arrival Rates of Organic Contaminants in Clean Rooms," *1993 Proceedings*, Vol 1, Institute of Environmental Sciences, Mount Prospect, IL, 1993, pp. 373–379.

[7] Liu, Y. A., and Fleming, R. H., "Reduced Electron Multiplier Dead Time in Ion Counting Mass Spectrometry," Review Science Instruments, Vol 64, 1993, p. 1661.

standard(s) and BLANK sample.

11.1.6.1 Confirm that the analytical sputter rate is such that each element monitored in a single profile is sampled at a frequency greater than or equal to once every 0.2 nm of sputtered depth.

11.1.6.2 If an oxygen jet is used, confirm that 0-leak pressure is suitable by measuring a matrix ion depth profile and demonstrating that matrix secondary ion yield is constant (within 20 %) during the analysis of the first 10 nm of a specimen. Perform this confirmation measurement on a typical specimen at the same sputter rate to be used for the measurement of the surface metal impurities. If the ion yield shows significant variation, increase the 0-leak pressure by a factor of 2X and reconfirm stability.

11.1.6.3 Depending upon the instrumentation used and if needed, measure the detector efficiency ratio(s) for any detectors used during the measurement (for example, the electron multiplier and the faraday cup detectors). Make this measurement by intercomparing standard secondary ion signals of the appropriate intensity (to minimize dead-time losses). The secondary ion count rates used here may be different for this measurement than for the analysis, and may be generated under different sputter rate conditions than the analysis.

11.2 *Analysis of Specimen*:

11.2.1 Center the primary ion beam, initialize the SIMS instrument control software, and begin a SIMS profile. For sodium, aluminum, potassium, and iron, the secondary ion signals generated by sputtering these contaminants from the free surface or native oxide layer on the specimen should ordinarily reach a maximum within the first 1 nm of the depth profile, and decrease monotonically thereafter. If this general profile shape is not obtained, repeat the measurement on a fresh surface of the specimen.

11.2.2 When the impurity signal has either: (*1*) decreased to at least <1 % of the maximum, (*2*) or has reached a constant background count rate, then measure and record the silicon matrix ion count rate on the appropriate detector.

11.2.3 Measure the sputter rate under the analysis conditions. This can be done by measuring the SIMS crater depth with a stylus profilometer or equivalent instrument if available, and combining the depth measurement with the recorded time elapsed during the sputter profile. If the analytical craters are too shallow to be measured by available instrumentation, the sputter rate must be monitored during a measurement series by repeated analysis of a previously characterized standard sample.

11.2.4 Measure the BLANK under the same analytical conditions as the unknown specimens.

12. Calculations

12.1 The RSF for an element in a matrix can be determined experimentally from the SIMS profile of a reference material containing a known areal density of the impurity of interest as follows:

$$\mathrm{RSF} = DNI_m t\,/d(SI_{\mathrm{i}\,-\,I_b}\,N) \qquad (1)$$

where:
D = the areal density of the impurity in atoms/cm^2,
N = the number of data cycles in the profile,
I_m = the matrix isotope secondary ion intensity, (counts/s),
d = the sputtered depth, cm,
SI_i = the sum of the impurity isotope secondary ion-counts over the depth of the profile,
I_b = a constant background intensity of the impurity isotope, and
t = the analysis time for the species of interest, s/cycle.

TABLE 1 Summary Statistics for Sodium (Units of 10^{10} Atoms/cm^2)

Sample	VPD/AAS	X-Bar	s_r	S_R	r	R
A	10–15	10.68	2.240	2.791	6.273	7.816
B	29–32	33.64	3.339	4.931	9.348	13.81
C	115–121	112.1	16.19	19.79	45.32	55.41
E	0.6–4	0.665	0.359	0.861	1.005	2.410

12.2 The calibration of concentration in a SIMS profile is calculated as follows:

$$C_i = I_i\,/I_m \times RSF \times (FC/EM) \qquad (2)$$

where:
C_i = the impurity atomic concentration, atoms/cm^3,
I_i = the isotope secondary in intensity, counts/s,
I_m = the matrix isotope secondary ion-intensity, counts/s,
RSF = in units of atoms/cm^3, and
FC/EM = the ratio of matrix intensities on the faraday cup (FC) to the electron multiplier (EM), when two detectors are used.

12.3 The conversion of data cycles or time into depth is completed by measuring the crater depth and the total time (or data cycles) of the sputtering that formed the crater. The depth scale is assumed to be linear with time or data cycles.

12.4 Calculate the RSFs and impurity concentration versus depth from Eq 1 and Eq 2.

12.5 Calculate the surface areal density by integrating the concentration versus depth profile after any subtraction of a constant background count rate that may be appropriate.

13. Report

13.1 Report the following information:

13.1.1 The instrument used, the operator, and the date of the measurements,

13.1.2 Identification of test, BLANK, and reference specimens,

13.1.3 Calibration procedure used,

13.1.4 Method used to discriminate molecular ion interferences,

13.1.5 Surface areal density of the impurity, and

13.1.6 Surface areal density of the impurity for the BLANK specimen.

14. Precision and Bias [8]

14.1 *Precision*—Table 1, Table 2 and Table 3 summarize the statistics from a spoke-wheel round robin including 4 test samples and 10 laboratories. Each laboratory was provided with a spin coated reference standard of surface sodium, aluminum, and potassium. The 95 % repeatability, *r*, and

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[8] Support data are available from ASTM Headquarters. Request RR: F01-1010.

TABLE 2 Summary Statistics for Aluminum (Units of 10^{10} Atoms/cm^{2})

Sample	VPD/AAS	X-Bar	s_r	S_R	r	R
A	3	3.504	0.6865	1.107	1.922	3.100
B	7–8	9.425	0.7684	2.239	2.152	6.269
C	22–25	28.80	2.298	6.107	6.434	17.10
E	not detected	0.795	0.390	0.760	1.093	2.128

TABLE 3 Summary Statistics for Potassium (Units of 10^{10} Atoms/cm^{2})

Sample	VPD/AAS	X-Bar	s_r	S_R	r	R
A	7–8	7.829	1.642	2.761	4.596	7.731
B	22–23	24.11	3.607	5.943	10.10	16.64
C	92	82.37	12.77	19.63	35.74	54.97
E	0.1–2	0.407	0.162	0.344	0.454	0.965

reproducibility, R, limits are calculated by 2.8 times their respective standard deviations (s_r, S_R).

14.1.1 SIMS measurements were made on samples taken from an iron contaminated silicon wafer to estimate the precision of the surface iron measurement. Two SIMS instruments were used: a CAMECA IMS 3f and a CAMECA IMS 4f. All measurements used a 3-keV oxygen ion beam with an oxygen flood. Measurements were taken over a one-year period. For the CAMECA IMS 3f, 23 measurements were taken with an average iron reading of 1.51×10^{11} atoms/cm^2 and a 1 standard deviation of 0.148×10^{11} atoms/cm^2. For the CAMECA IMS 4f, 20 measurements were taken with an average iron reading of 1.71×10^{11} atoms/cm^2 and 1 standard deviation of 0.188×10^{11} atoms/cm^2.

14.2 *Bias*—Bias cannot be estimated because there are no accepted absolute standards. However, for comparison only, the VPD/AAS results for the sodium, aluminum, and potassium test samples are included in Tables 1-3. A correlation between SIMS and TXF quantitive results for iron is shown[9].

15. Keywords

15.1 aluminum; iron; potassium; silicon; SIMS; sodium; surface contamination

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[9] Smith, S. P., and Metz, J., "Understanding the Correlation of Surface SIMS and TXRF Measurements of Surface Metal Contamination on Silicoan Wafers," Science and Technology of Semiconductor Surface Preparation, edited by G. S. Higashi, M. Hirose, S. Raghavan, and S. Verhaverbeke, *Material Research Society Symposium Proceedings*, Vol 477, Materials Research Society, Pittsburgh, PA, l997, pp. 305–310.