13.3 If a wafer map was made, report the following information in addition to a density plot of the carrier recombination lifetime:

13.3.1 Point spacing and pattern, and

13.3.2 Radius of the mapped area.

13.4 If measurements were made at a specific or several temperatures, report the temperature of each measurement.

14 Precision and Bias

14.1 *Precision* — Neither the intralaboratory nor the interlaboratory precision of this test method has yet been established. In spite of this limitation, the technique is widely utilized in the industry without the benefit of standardization of the test conditions. Because of the lack of a precision determination, this test method should be used for materials specification and acceptance only after the parties to the test have established reproducibility and correlation.

14.2 *Bias* — No information can be presented on the bias of this test method because no material having an accepted reference value of carrier recombination lifetime is available.

15 Keywords

15.1 contactless measurement; microwave reflection; photoconductivity decay; recombination lifetime; silicon wafers

RELATED INFORMATION 1
INJECTION LEVEL CONSIDERATIONS

NOTICE: This related information is not an official part of SEMI MF1535. It was derived from information developed during the original preparation of the standard in ASTM Committee F-1 in 1994. This related information was approved for publication by full letter ballot procedures.

R1-1 The carrier recombination lifetime is frequently associated with the minority carrier lifetime. This association is correct only if the lifetime is determined for low injection level when η (the ratio of density of excess photogenerated carriers to the equilibrium density of majority carriers) is much less than 1, and then only if certain other conditions are also met (see Related Information 2 and Related Information 3). Nevertheless, the low-injection (small-signal) value of the carrier recombination lifetime is independent of the exact value of η provided that $\eta \ll 1$. However, in this test method, it is often neither possible nor convenient to make measurements in the low-injection regime. When this is the case, the measured recombination lifetime is a function of the injection level.

R1-2 The basic model for carrier recombination through defect centers in semiconductors was developed independently by Hall[14] and by Shockley and Read.[15] This model has been thoroughly discussed by Blakemore.[16] In the Shockley-Read-Hall (S-R-H) model, it is assumed (1) that the doping level of the semiconductor is not so high that the semiconductor becomes degenerate, and (2) that the density of defect centers is small compared with the majority carrier density.

NOTE 1: The reader should refer to Blakemore's text for a more complete treatment than is presented here, including the derivation of the S-R-H expression (Equation R1-1) for carrier lifetime and discussion of the effect of Fermi energy on the small-signal recombination lifetime. In addition, Blakemore goes on to discuss other complexities that result when the density of defect centers is not small compared with the majority carrier density,[17] and when carrier trapping occurs.[18]

R1-3 Both the assumptions underlying the S-R-H model are generally appropriate for the specimens to be measured by this test method. With these assumptions, the density of excess electrons (n_e) is equal to the density of excess holes (p_e), and the electron (τ_n) and hole (τ_p) lifetimes for recombination through a defect

center located at an energy ε_T within the forbidden energy gap are equal. This carrier recombination lifetime, τ, in μs, is given as follows:

$$\tau = \tau_n = \tau_p = \frac{\tau_{n0}(p_0 + p_1 + n_e) + \tau_{p0}(n_0 + n_1 + n_e)}{(n_0 + p_0 + n_e)} \quad \text{(R1-1)}$$

where:

τ_{n0} = time constant for capture of an electron in an empty center, in μs,

τ_{p0} = time constant for capture of a hole in a filled center, in μs,

n_0 = equilibrium density of electrons in a nondegenerate semiconductor, in electrons/cm^3,

p_0 = equilibrium density of holes in a nondegenerate semiconductor, in holes/cm^3,

n_1 = density of electrons in a nondegenerate semiconductor when the Fermi energy, ε_F, = ε_T, in electrons/cm^3, and

p_1 = density of holes in a nondegenerate semiconductor when the Fermi energy, ε_F, = ε_T, in holes/cm^3.

R1-4 In the low-injection limit, n_e can be neglected and Equation R1-1 reduces to the small-signal recombination lifetime, τ_0.

$$\tau_0 = \tau_{n0}\frac{(p_0 + p_1)}{(p_0 + n_0)} + \tau_{p0}\frac{(n_0 + n_1)}{(n_0 + p_0)} \quad \text{(R1-2)}$$

On the other hand, in the high-injection limit, n_e is the dominant term and the recombination lifetime becomes:

$$\tau_\infty = \tau_{n0} + \tau_{p0} \quad \text{(R1-3)}$$

At intermediate injection levels the recombination lifetime can be expressed as a combination of τ_0 and τ_∞:

$$\tau = \frac{(n_0 + p_0)\tau_0 + n_e\tau_\infty}{n_0 + p_0 + n_e} = \frac{\tau_0 + \eta\tau_\infty}{1+\eta} \quad \text{(R1-4)}$$

Therefore, a straight line is obtained when the quantity $\tau(1+\eta)$ is plotted against η. The zero intercept of this line is τ_0 and its slope is τ_∞. The linearity of this function provides a test for the validity of the S-R-H model and also for the presence of multiple defect centers in the test specimen.

14 Hall, R. N., "Electron-Hole Recombination in Germanium," *Phys. Rev.* **87**, 387 (1952).

15 Shockley, W., and Read, W. T., "Statistics of the Recombination of Holes and Electrons," *Phys. Rev.* **87**, 835–842 (1952).

16 Blakemore, J. S., *op. cit.*, Section 8.3.

17 Blakemore, J. S., *op. cit.*, Sections 8.4 and 8.5.

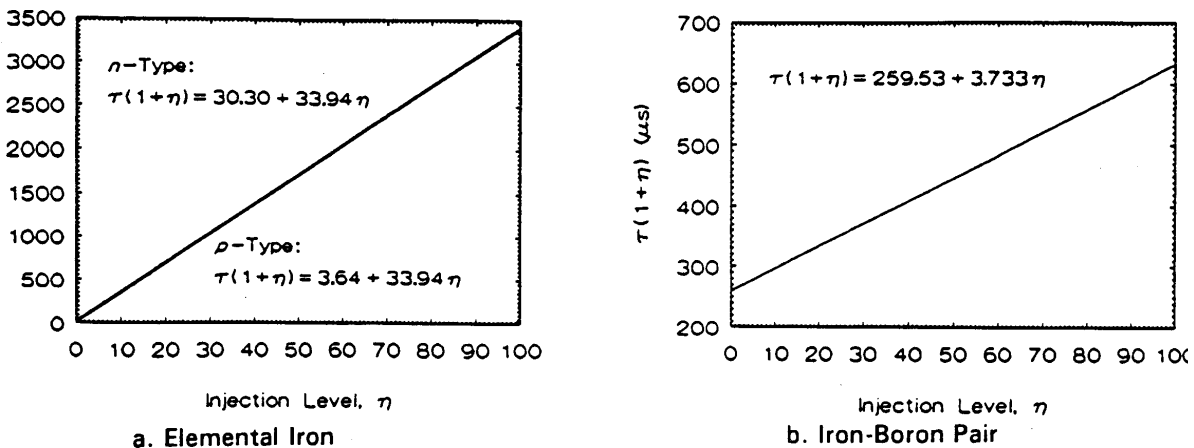18 Blakemore, J. S., *op. cit.*, Section 8.2.

a. Elemental Iron

b. Iron-Boron Pair

Figure R1-1
Derivation of τ_0 and τ_∞ from Plots of Recombination Lifetime versus Injection Level

Table R1-1 Parameters Used for Calculation of Recombination Lifetime versus Injection Level

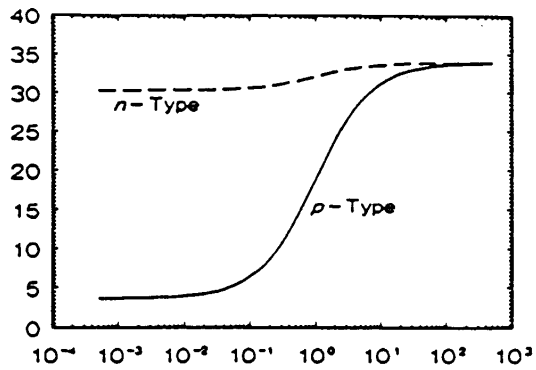| *Parameter*	*Elemental Iron (Fe)*	*Iron-Boron (Fe-B)*
Temperature, K	300	300
Boron density (p_0), cm^{-3}	1×10^{15}	1×10^{15}
n_0, cm^{-3}	1.16×10^5	1.16×10^5
Iron density, atoms/cm^3	5×10^{11}	5×10^{11}
Defect energy, eV (above valence band edge)	0.400	0.100
τ_{n0}, µs	3.64	0.400
τ_{p0}, µs	30.3	3.33
n_1, cm^{-3}	1.96×10^7	179
p_1, cm^{-3}	5.91×10^{12}	6.48×10^{17}

R1-5 This linearity is illustrated in Figure R1-1 for recombination through the elemental iron defect center in both *n*- and *p*-type silicon and through iron-boron pairs in *p*-type silicon.   The parameters for the calculations are listed in Table R1-1; in each case it is assumed that all of the iron is in the defect state listed. Note that for elemental iron in *p*-type silicon, $\tau_0 = \tau_{n0}$, for the iron-boron pair, $\tau_0 \gg \tau_{n0}$; and for elemental iron in *n*-type silicon, $\tau_0 = \tau_{p0}$.

R1-6 Injection level spectroscopy, which has been proposed[3] as a method for identifying impurity levels, relies on the relationship between τ_0 and τ_∞ as a function of the density of the impurity center for specific doping conditions. This method is particularly useful for studying iron in p -type silicon because of the facts that (*1*) it is possible to treat the sample to ensure that essentially all of the iron is in either the elemental or paired state,[19] and (*2*) the injection level dependence is markedly different for the two species (see Fig. R1-2).
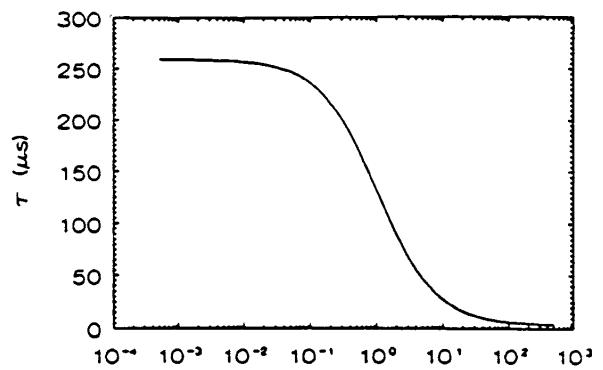
R1-7 However, it should be noted that if several contaminants are present at the same time at similar concentrations, the measured ratio of τ_0 to τ_∞ may represent some average of the values for the various contaminants because this technique is not impurity specific as is deep-level transient spectroscopy or other spectroscopic techniques involving filling and emptying of defect centers in the space-charge layer.

19 Zoth, G., and Bergholz, W., "A Fast, Preparation-Free Method to Detect Iron in Silicon," *J. Appl. Phys.* **67**, 6764–6771 (1990).

Figure R1-2
Recombination Lifetime as a Function of Injection Level

RELATED INFORMATION 2
TEMPERATURE DEPENDENCE OF CARRIER RECOMBINATION LIFETIME

NOTICE: This related information is not an official part of SEMI MF1535. It was derived from information developed during the original preparation of the standard in ASTM Committee F-1 in 1994. This related information was approved for publication by full letter ballot procedures.

R2-1 The temperature dependence of the carrier recombination lifetime as determined under low-injection conditions has been proposed[4] as a means for identifying metallic impurities in silicon. However, this is possible only for low injection and then only under very restricted conditions.

R2-2 In the low-injection limit, the (S-R-H) carrier recombination lifetime is given by Equation R1-2. In a nondegenerate semiconductor, the carrier densities, n_0, p_0, n_1, and p_1, are all exponential functions of temperature. The equilibrium electron and hole densities, n_0 and p_0, respectively, are given as follows:

$$n_0 = N_c \exp\left(\frac{\varepsilon_F - \varepsilon_c}{kT}\right) \text{ and } p_0 = N_v \exp\left(\frac{\varepsilon_v - \varepsilon_F}{kT}\right) \quad \text{(R2-1)}$$

where:

N_c = the density of states in the conduction band, in states/cm^3,

N_v = density of states in the valence band, in states/cm^3,

ε_F = Fermi energy, or the equilibrium electrochemical potential, in eV,

ε_c = conduction band edge, in eV,

ε_v = valence band edge, in eV,

k = Boltzmann's constant ($= 8.6173 \times 10^{-5}$ eV/K), and

T = temperature, in K.

Similarly, the electron (n_1) and hole (p_1) densities when the Fermi energy is at the defect center energy ε_T are given as follows:

$$n_1 = N_c \exp\left(\frac{\varepsilon_T - \varepsilon_c}{kT}\right) = n_0 \exp\left(\frac{\varepsilon_T - \varepsilon_F}{kT}\right)$$

and

$$p_1 = N_v \exp\left(\frac{\varepsilon_v - \varepsilon_T}{kT}\right) = p_0 \exp\left(\frac{\varepsilon_F - \varepsilon_T}{kT}\right) \quad \text{(R2-2)}$$

R2-3 From Equation R1-2, it is clear that the low-injection (or small-signal) carrier recombination lifetime, τ_0, can be calculated readily in terms of the electron and hole capture time constants, τ_{n0} and τ_{p0}, as the sum of four terms:

$$\tau_0 = \frac{\tau_{n0} p_0}{p_0 + n_0} + \frac{\tau_{n0} p_1}{p_0 + n_0} + \frac{\tau_{p0} n_0}{p_0 + n_0} + \frac{\tau_{p0} n_1}{p_0 + n_0} \quad \text{(R2-3)}$$

In the temperature region between the freeze-out region and the intrinsic region where the majority carrier density is equal to the net dopant density, the denominator of these terms is constant. If, in addition, the capture time constants are assumed not to depend on temperature, the slope of the $\ln \tau_0$ versus $1/T$ curve yields the defect center energy, ε_T, in those temperature regions where the defect centers are partially filled (that is, when a term in p_1 or n_1 dominates the small-signal recombination lifetime). Although this assumption is usually not rigorously correct, the variation of capture time constant with temperature is usually much less strong than the exponential dependence of the carrier densities.

R2-4 Three examples, elemental iron in both n- and p-type silicon and iron-boron pairs in p-type silicon, serve to illustrate these considerations. In each case the iron density is assumed to be 5×10^{11} atoms/cm^3 and the dopant density is assumed to be 1×10^{15} atoms/cm^3, for p-type silicon this dopant density corresponds to a resistivity $\rho \approx 10$–15 Ω·cm and for n-type silicon it corresponds to a resistivity $\rho \approx 3$–5 Ω·cm. The temperature range considered is from 250 to 1000 K over which the dopant atoms may be assumed to be fully ionized. Elemental iron is a donor center which, as shown in Table R1-1, lies well above the valence band edge in the bottom half of the forbidden energy gap. The iron-boron pair is also a donor center but it lies much closer to the top of the valence band. Consequently, in each case $p_1 \gg n_1$, the difference being greater for the iron-boron pair.

R2-4.1 *Elemental Iron in p-Type Silicon* (see Figure R2-1) — Below room temperature, $p_0 \gg p_1 \gg n_1 \gg n_0$, so $\tau_0 = \tau_{n0}$. Between about 150°C and about 200°C, $p_1 > p_0 > n_0$ and the term p_1 is the largest single term. However, because there is not much difference between p_1 and p_0, the slope of the τ_0 curve never quite reaches that of the p_1 term, and thus the energy of the elemental iron center cannot be determined accurately from the curve. At still higher temperatures, n_0 becomes
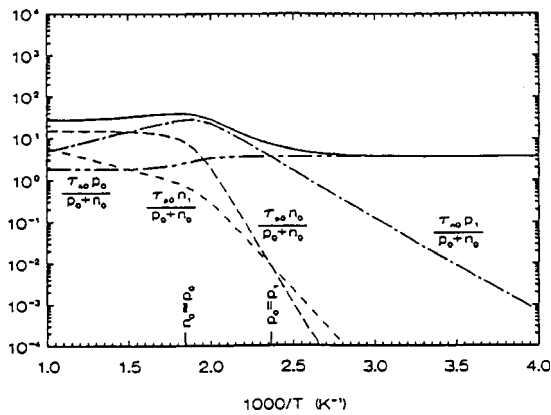
Figure R2-1
Low-Injection Recombination Lifetime
(solid curve) as a Function of Reciprocal
Temperature for Elemental Iron in
***p*-Type Silicon**

Figure R2-2
Low-Injection Recombination Lifetime
(solid curve) as a Function of Reciprocal
Temperature for Elemental Iron in
***n*-Type Silicon**

comparable with p_0 (approaching the intrinsic condition) and the carrier recombination lifetime decreases; however, no single term dominates the expression and so the slopes have no physical meaning.

R2-4.2 *Elemental Iron in n-Type Silicon* (see Figure R2-2) — Below about 100°C, $n_0 \gg p_1 \gg n_1 \gg p_0$, so $\tau_0 = \tau_{p0}$. Between about 200°C and about 225°C, $p_1 > n_0 > p_0$ and the term p_1 is again the largest single term. In this case, there is even less difference between the terms in p_1 and p_0, so the slope of the τ_0 curve is never dominated by a single term, and thus the energy of the elemental iron center cannot be determined from the curve. At still higher temperatures, p_0 becomes comparable with n_0 (approaching the intrinsic condition) and the carrier recombination lifetime decreases; however, as for near-intrinsic *p*-type material, no single term dominates the expression and so the slopes have no physical meaning.

R2-4.3 *Iron-Boron Pairs in p-Type (Boron-Doped) Silicon* (see Figure R2-3) — In this case, $p_1 \gg p_0 \gg n_0 \gg n_1$, so that the term in p_1 dominates the low-injection recombination lifetime at all temperatures from well below room temperature to about 225°C. Since $p_0 = N_{\text{boron}}$, $\tau_0 \approx \tau_{n0}$ (p_1/N_{boron}), so that the negative slope of a plot of $\ln \tau_0$ against $1/T$ yields $\Delta\varepsilon = \varepsilon_{\text{Fe–B}} - \varepsilon_v$, the activation energy of the iron-boron pair. At higher
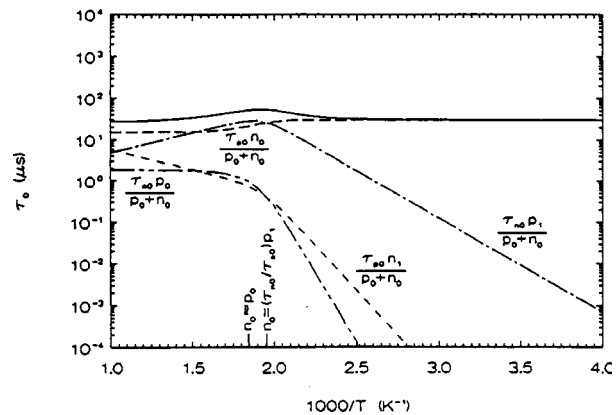
temperatures, the material becomes near-intrinsic and the denominator increases, resulting in a decrease in τ_0.

R2-5 These examples illustrate the limited range of conditions over which the activation energy obtained from measurements of carrier recombination lifetime as a function of temperature slightly above room temperature can be associated with the energy level of a defect center located near the middle of the forbidden energy gap, as are most of the elemental metallic impurities.
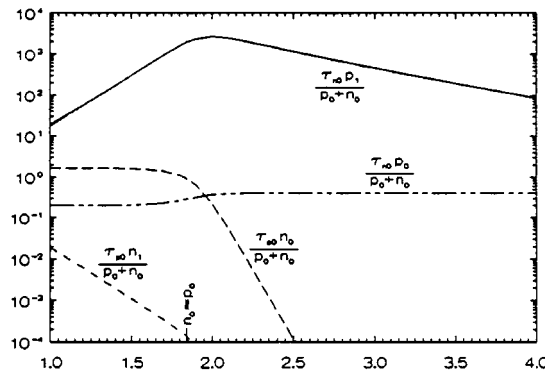

Figure R2-3
Low-Injection Recombination Lifetime (solid curve)
as a Function of Reciprocal Temperature for Iron-
Boron in *p*-Type Silicon

RELATED INFORMATION 3
MINORITY-CARRIER RECOMBINATION LIFETIME

NOTICE: This related information is not an official part of SEMI MF1535. It was derived from information developed during the original preparation of the standard in ASTM Committee F-1 in 1994. This related information was approved for publication by full letter ballot procedures.

R3-1 The recombination of an excess electron-hole pair at a defect center is a two-step process. It involves either (*a*) the capture of an electron in an empty defect center followed by the capture of a hole or (*b*) the capture of a hole on a filled defect center followed by the capture of an electron. Thus, the recombination time depends on the number of filled or empty defect centers as well as the capture time constants.

R3-2 The occupancy of the defect centres is controlled by the position of the Fermi energy as discussed by Blakemore.[16] If all of the defect centers are empty, the electron recombination time is governed by the electron capture time constant, τ_{n0}; this occurs when the Fermi energy is well below the defect center energy. If all of the defect centers are filled, the hole recombination time is governed by the hole capture time constant, τ_{p0}; this occurs when the Fermi energy is well above the defect energy. Since the position of the Fermi energy is governed primarily by the dopant density, the occupancy of the defect centers may be different for different resistivity wafers.

R3-3 There are two sets of equivalent cases. The defect center may be in the same half of the forbidden gap as the Fermi energy or it may be in the other half. Thus, the case for the defect center in the lower half of the gap of a *p*-type semiconductor is the same as for the defect center in the upper half of the gap in an *n*-type semiconductor with the roles of electrons and holes interchanged. Similarly, the case for the defect center in the upper half of the gap in a *p*-type semiconductor is the same as for the defect center in the lower half of the gap in an *n*-type semiconductor.

R3-4 As examples, consider the three cases of elemental iron in both *n*- and *p*-type silicon and iron-boron pairs in *p*-type silicon at room temperature (300 K). In each case the iron density is assumed to be 5×10^{11} atoms/cm^3. Note that at for very low resistivity wafers, the nondegeneracy requirement of the S-R-H model may be violated.

R3-4.1 *Elemental Iron in p-Type Silicon* (see Figure R3-1) — For all practical values of resistivity, the Fermi energy lies many *kT* below the near mid-gap energy of the elemental iron center. Consequently, the defect centers are empty and the limiting process is capture of excess minority electrons, there being ample numbers of holes present to recombine with the electron immediately upon its capture by the defect center. Therefore, the small-signal carrier recombination lifetime is equal to the electron (minority-carrier) capture time constant: $\tau_0 = \tau_{n0}$.

R3-4.2 *Elemental Iron in n-type Silicon* (see Figure R3-2) — In this case, for all values of resistivity, the Fermi energy is very far above the defect center energy and all the defect centers are filled, and hole capture is governed by the hole capture time constant, τ_{p0}. Because the Fermi energy is close to the conduction band edge, there are large numbers of electrons present so that as soon as a hole is captured, the defect center is filled again. Therefore, hole capture is the limiting process, and the small-signal carrier recombination lifetime is equal to the hole (minority-carrier) capture time constant: $\tau_0 = \tau_{p0}$.

R3-4.3 *Iron-Boron Pairs in p-Type (Boron-Doped) Silicon* (see Figure R3-3) — This defect center is located quite close to the valence band edge. For all but very low resistivity wafers, the Fermi energy lies above the defect center energy so that some of the defect centers are filled. In this case, the capture of minority electrons is still the limiting process, but since only a fraction of the sites can capture an electron, the small-signal recombination lifetime is larger than the electron capture time constant. Quantitatively, because $n_0 << p_0$, the small-signal carrier recombination lifetime is given by $\tau_0 = \tau_{n0}(p_1/p_0)$.

R3-4.4 The fourth possible case is one in which the defect center is located near valence band edge in *n*-type material. The iron-boron pair, of course, cannot exist in *n*-type material; however, for the case of a hypothetical defect center with energy near the valence band in *n*-type material, $\tau_{n0}p_1 >> \tau_{p0}n_0$ for all but the most heavily doped material so this term dominates the small-signal lifetime and the minority-carrier properties do not influence the recombination process.

R3-5 Thus, for deep lying defect centers, the low-injection (small-signal) carrier recombination lifetime is equal to the minority-carrier capture time constant (or minority-carrier lifetime), while for centers close to the band edge, the small-signal carrier recombination lifetime can be much larger than the minority-carrier capture time constant.
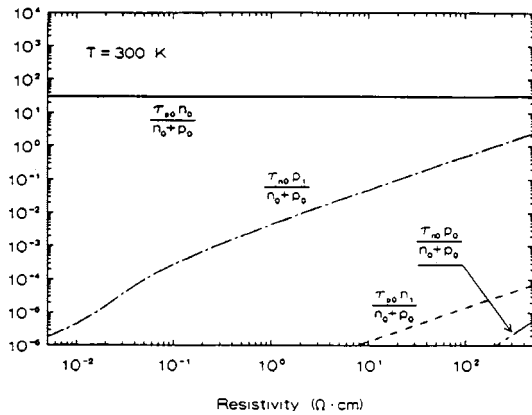
Figure R3-1
Low-Injection Recombination Lifetime (solid curve) as a Function of Resistivity for Elemental Iron in *p*-Type Silicon at Room Temperature
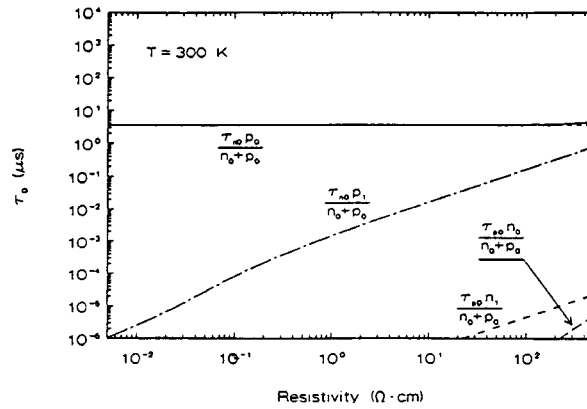

Figure R3-2
Low-Injection Recombination Lifetime (solid curve) as a Function of Resistivity for Elemental Iron in *n*-Type Silicon at Room Temperature
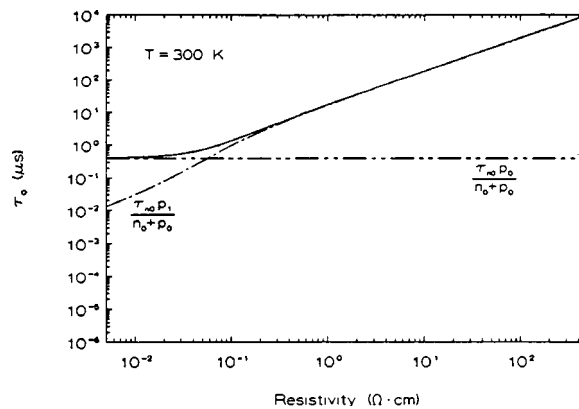

Figure R3-3
Low-Injection Recombination Lifetime (solid curve) as a Function of Resistivity for Iron-Boron Pairs in *p*-Type Silicon at Room Temperature

NOTICE: SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature, respecting any materials or equipment mentioned herein. These standards are subject to change without notice.

By publication of this standard, Semiconductor Equipment and Materials International (SEMI) takes no position respecting the validity of any patent rights or copyrights asserted in connection with any items mentioned in this standard. Users of this standard are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights are entirely their own responsibility.

SEMI MF1569-0705
GUIDE FOR GENERATION OF CONSENSUS REFERENCE MATERIALS FOR SEMICONDUCTOR TECHNOLOGY

> This guide was technically approved by the global Silicon Wafer Committee. This edition was approved for publication by the global Audits and Reviews Subcommittee on April 7, 2005. It was available at www.semi.org in June 2005 and on CD-ROM in July 2005. Original edition published by ASTM International as ASTM F 1569-94. Last previous edition SEMI MF1569-94 (Reapproved 1999).

1 Purpose

1.1 This guide covers the procedures for producing a single set of consensus reference materials (ConRefs) in the absence of suitable certified reference materials from an established source.

1.2 Such reference materials are frequently required for calibration of measurement systems to reduce bias differences between different organizations.

1.3 The generated ConRefs can be used by a single laboratory for internal use or for interlaboratory comparison of related equipment and materials.

1.4 Most often, however, they are used for replicating multiple sets of reference materials. In such a case, the property values of these reference materials are traceable to the values of the property value of the ConRefs. Depending on the nature of the preparing organization, these multiple sets may be certified reference materials or working reference materials. For this purpose, a guide for generation of reference materials specific to the materials and property may be required; Appendix 1 outlines the requirements for preparing a guide for generation of multiple sets of reference materials.

2 Scope

2.1 This guide covers the steps to be taken to generate a set of ConRefs for a specific property or family of related properties required in semiconductor technology.

2.2 The procedure for generating the set of ConRefs is based on interlaboratory testing in accordance with ASTM Practice E 691. It is assumed for the purposes of this guide that the test method evaluated by the interlaboratory study (ILS) is appropriate for determining the property values of the ConRef.

2.3 This guide does not cover the selection of one of several possible test methods nor does it cover the case for which other reference materials must be used in the measurement of the properties of the ConRef.

2.4 This guide also describes procedures that may be used to generate consensus property values that may form the basis for the generation of multiple sets of CRMs or reference materials (RMs).

NOTICE: This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health guides and determine the applicability of regulatory or other limitations prior to use.

3 Referenced Standards and Documents

3.1 *ASTM Standards*

E 456 — Terminology Relating to Quality and Statistics[1]

E 691 — Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[1]

3.2 *ISO Standards*

ISO Guide 30:1981 — Terms and Definitions Used in Connection with Reference Materials[2]

---

1 *Annual Book of ASTM Standards,* Vol 14.02, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Telephone: 610-832-9500, Fax: 610-832-9555, Website: www.astm.org.

ISO 8402 — Quality—Vocabulary[2]

ISO 10012-1 — Quality Assurance Requirements for Measuring Equipment—Part 1: Management of Measuring Equipment[2]

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

4 Terminology

4.1 *Definitions*

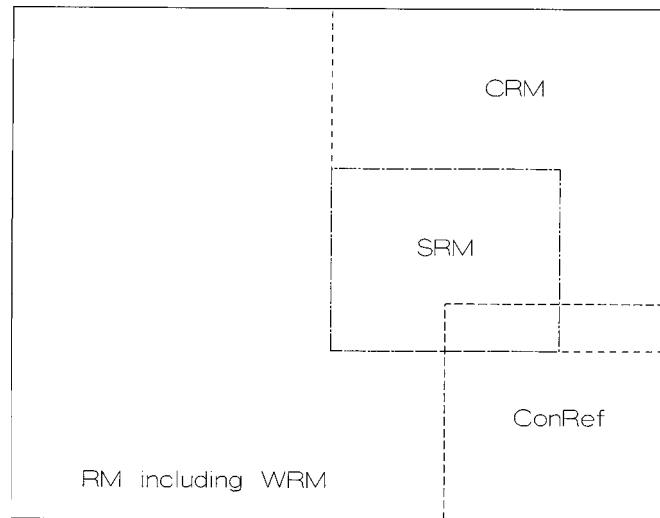NOTE 1: See Figure 1 for a schematic presentation of the hierarchy of reference materials.

Figure 1
Reference Material Hierarchy

4.1.1 *certified reference material (CRM)* — a reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation that is issued by a certifying body (ISO Guide 30:1981).

4.1.2 *consensus reference material (ConRef)* — a reference material one or more of whose property values have been established by a documented ILS that is based on a technically valid test method.

4.1.3 *reference material (RM)* — a material or substance one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, (for) the assessment of a measurement method, or for assigning values to materials (ISO Guide 30:1981; ISO 10012-1).

4.1.3.1 *Discussion* — A reference material made by a laboratory for its own use is referred to as a working reference material (WRM). This term is gradually replacing the term, secondary reference material, which has been used widely in the past.

4.1.4 *Standard Reference Material (SRM[3])* — a certified reference material issued by the U.S. National Institute of Standards and Technology.

4.1.5 *traceability* — the ability to trace the history, application, or location of an item or activity, or similar items or activities, by means of recorded identification (ISO 8402).

4.1.5.1 *Discussion* — ISO 8402 states that in a calibration sense, traceability relates measuring equipment to national or international standards, primary standards, or basic physical constants or properties. In this guide, as in

---

2 International Organization for Standardization, ISO Central Secretariat, 1, rue de Varembé, Case postale 56, CH-1211 Geneva 20, Switzerland. Telephone: 41.22.749.01.11; Fax: 41.22.733.34.30, Website: /www.iso.ch; available in the U.S. from American National Standards Institute, New York, NY 10036, USA. Telephone: 212.642.4900, Fax: 212.398.0023, Website: www.ansi.org.

3 SRM® is a registered trademark of the U.S. National Institute of Standards and Technology and the U.S. Government.

ISO 10012-1, the term "measuring equipment" is extended to include both measuring instruments and measurement standards (including reference wafers).

4.2 Terminology related to the conduct and analysis of the ILS may be found in ASTM Terminology E 456 and ASTM Practice E 691.

5 Summary of Guide

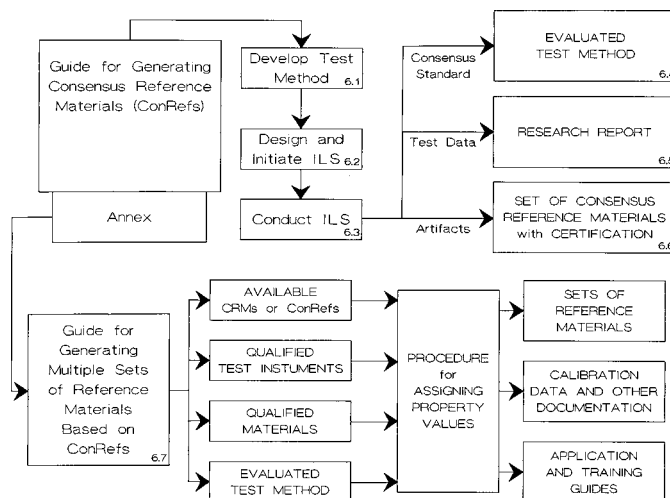NOTE 2: See Figure 2 for a flow chart of the steps covered.

Figure 2
Flow Chart for Generation of Consensus Reference Materials and Derived Sets of Reference Materials

5.1 The test method to be used is selected or developed, and acceptable levels of repeatability and reproducibility are defined.

5.2 An ILS test protocol for use with the selected consensus test method is developed in accordance with ASTM Practice E 691 and the proper materials and instrumentation are assembled.

5.3 The ILS is executed and analyzed.

5.4 The results are evaluated against the criteria selected in ¶5.1. If the results are acceptable, a precision statement is developed and balloted for inclusion in the test method. If the results are not acceptable, the test method validity and the usefulness of the materials tested are assessed.

5.5 The results are incorporated into a research report.

5.6 If the results are acceptable, the materials used in the test are now qualified as ConRefs. They have values of the desired property (or properties) that represent the consensus of the industry; the uncertainty in these values can be estimated from the repeatability and reproducibility obtained in the test, as documented in the research report. These materials are stored in a location accessible for future use in preparing replicate sets of reference materials.

6 Procedure

6.1 Select or establish the test method to be used and define acceptable levels of repeatability and reproducibility for the proposed test method.

6.1.1 If the test method has already been evaluated by an interlaboratory study (ILS) and contains repeatability and reproducibility results documented in a research report or in the method itself, proceed directly to ¶6.4. Otherwise develop the test method as follows:

6.1.1.1 Determine feasibility of proposed test method.

6.1.1.2 Conduct screening experiments (ruggedness tests) of the proposed test method in a single laboratory.

6.1.1.3 Draft test method.

6.1.1.4 Obtain consensus within a representative task group or subcommittee.

6.2 *Design and initiate the Interlaboratory Study (ILS).*

6.2.1 Design the experiment in accordance with the principles of ASTM Practice E 691, taking into account whether the test is destructive or nondestructive.

6.2.2 Prepare an interlaboratory test protocol that specializes the test method to this design and also includes a provision for reporting deviations from the method if participants in the interlaboratory test are unable to follow the test method exactly.

6.2.3 Select, qualify, and prepare materials for the interlaboratory test, paying particular attention to issues of uniformity, stability, storage, transportation, and handling.

6.2.4 Qualify instrumentation in accordance with test method and applicable quality control practices.

6.2.5 Select and qualify participating laboratories.

6.3 *Execute the interlaboratory experiment.*

6.3.1 Collect the data in a round-robin or hub-and-spoke mode.

6.3.2 Analyze the data collected in accordance with Practice E 691 to establish the repeatability and reproducibility of the test.

6.3.3 Derive an appropriate "uncertainty" from the results of the analysis and incorporate the repeatability and reproducibility into "Precision" and "Bias" sections for the test method.

6.4 *Evaluate test results against the preselected criteria (see ¶6.1).*

6.4.1 If the result is acceptable, proceed to ¶6.5.

6.4.2 If the result is not acceptable, assess the validity of the test method and the usefulness of the generated materials. Consider whether the test method may need to be revised or the ILS repeated with improved controls on the procedures used.

6.5 *Prepare a Research Report.*

6.5.1 Include the following information in the research report:

6.5.1.1 Description of the nature, purpose, and application of the ILS.

6.5.1.2 Identification of the test method evaluated.

6.5.1.3 Detailed instructions for carrying out the test method including any special conditions or requirements for the test and any special requirements regarding the nature, transmission, and storage of the test materials.

6.5.1.4 List of participating laboratories.

6.5.1.5 Data report forms.

6.5.1.6 Statistical data summary.

6.5.1.7 Summary of results and conclusions.

6.5.2 Reference the research report in the appropriate test method.

6.5.3 Consider preparing a technical paper to report the results of the ILS.

6.6 Determine disposition of materials.

6.6.1 If the results of the ILS are considered acceptable, establish an appropriate repository for the ConRefs generated.

6.6.2 Establish the protocol for storage and handling of the ConRefs and the ground rules for future use in developing other reference materials.

6.7 Prepare guide for generation of multiple sets of reference materials traceable to the ConRefs generated by the ILS (see Appendix 1).

7 Keywords

7.1 certified reference material; consensus reference material; flat panel display; interlaboratory experiment; reference material; semiconductor; silicon; sputtering target; working reference material

APPENDIX 1
GENERATION OF MULTIPLE SETS OF REFERENCE MATERIALS

NOTICE: The material in this appendix is an official part of SEMI MF1569. Approval was by full letter ballot procedures with publication authorized by the ISC Audits & Review Subcommittee on April 7, 2005.

A1.1 This guide describes a methodology for generating a single set of reference materials from a test procedure. Replication of this set requires additional procedures for generating multiple sets of reference materials from other materials such as the ConRefs. Therefore, another procedure is required; this procedure is of the type used by laboratories that generate certified reference materials and is generally specific to the particular material or property.

A1.2 The guide for generation of multiple sets of reference materials should include information on the following topics:

A1.2.1 Terminology specific to the property or material,

A1.2.2 Reagents as needed for preparation of the materials,

A1.2.3 Hierarchy of available reference materials including CRMs and ConRefs,

A1.2.4 Description of test instrumentation,

A1.2.5 Qualification of test instrumentation,

A1.2.6 Selection and qualification of materials,

A1.2.7 Preparation of materials,

A1.2.8 Procedures for assigning property values,

A1.2.9 Deliverable documentation,

A1.2.10 Application of the reference materials,

A1.2.11 Operator training for generation or use (or both) of the reference materials, and

A1.2.12 Keywords.

A1.3 Include test analyses and raw data values in related information sections, as required.

SEMI MF1617-0304
TEST METHOD FOR MEASURING SURFACE SODIUM, ALUMINUM, POTASSIUM, AND IRON ON SILICON AND EPI SUBSTRATES BY SECONDARY ION MASS SPECTROMETRY

1 Purpose

1.1 Secondary ion mass spectrometry (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.

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

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

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

1.5 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.

2 Scope

2.1 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 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.

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

2.3 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.

2.4 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.

2.5 This test method is complementary to:

2.5.1 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.

2.5.2 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.

NOTICE: This standard does not purport to address safety issues, 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 or other limitations prior to use.

3 Limitations

3.1 Surface metal contamination of sodium, aluminum, potassium or iron introduced during handling of the test specimen or during the measurement itself introduces 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.)

3.1.1 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$_2$H$_3^+$ 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.

3.1.2 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.[1]

3.1.3 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.

3.1.4 The $^{54}Fe^{+1}$ signal can have interferences from $^{27}Al_2^{+1}$ or $^{54}Cr^{+1}$.

3.1.5 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.[2]

3.2 Bias in the relative sensitivity factors (RSFs) derived from reference materials can introduce bias into the SIMS measured areal densities.

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

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

3.5 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.

3.6 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.

3.7 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.

4 Referenced Standards

4.1 *ASTM Standards*

E 122 — Practice for Choice of Sample Size to Estimate a Measure of Quality for a Lot or Process [3]

E 673 — Terminology Relating to Surface Analysis[4]

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

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

6 Summary of Test Method

6.1 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.

6.2 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).

6.3 The area of analysis may be different for different instruments and may range from 100 μm $\times$ 100 μm to 1 mm $\times$ 1 mm.

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

6.5 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.

6.6 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 multiple detectors are used during the test, the relative sensitivities of the detectors are determined by measuring standard ion signals (either the same positive

---

1 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.

2 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 Volume 94-9, edited by D. N. Schmidt (The Electrochemical Society, Pennington, NJ, 1994) pp. 339–350.

3 *Annual Book of ASTM Standards*, Vol 14.02, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Telephone: 610-832-9500, Fax: 610-832-9555, Website: www.astm.org

4 *Annual Book of ASTM Standards*, Vol 03.06.

secondary ion count rate or ion count rates of known relative intensity such as natural $^{28}Si/^{30}Si$) on each detector.

6.7 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 RSFs measured from reference materials.[34]

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 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 1: 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 ASTM Practice E 122 for suggested choices of sampling plans.

9 Specimen Requirements

9.1 Sample specimen surfaces must be flat and smooth (see Sections 3.5 and 3.6).

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 2: 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[5]; 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

5 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.

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 to be used in Equation 1 (see Section 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 to be used in Equation 1 (see Section 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.

10.1.1.3 *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 to be used in Equation 1 (see Section 12.1) is the implanted isotopic dose.

11 Procedure

11.1 *Specimen Loading 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%.[6]

11.1.6 Confirm that analytical conditions are appropriate to the measurement goals by measurement of known reference 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 2× 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

---

6 Liu, Y. A., and Fleming, R. H., "Reduced Electron Multiplier Dead Time in Ion Counting Mass Spectrometry," *Rev. Sci. Instr*, **64**, 1661 (1993).

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 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:

$$RSF = \frac{DNI_m t}{d(SI_i - I_b N)} \qquad (1)$$

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.

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

$$C_i = \frac{I_i}{I_m} RSF \left(\frac{FC}{EM} \right) \qquad (2)$$

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   =   relative sensitivity factor, atoms/cm^3, and

$\frac{FC}{EM}$ =   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 Equations 1 and 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[7]

14.1 *Precision* — Tables 1, 2, and 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 reproducibility, *R*, limits are

---

7 Support data are available from SEMI Headquarters. Request SEMI MF1617 round robin report (formerly ASTM RR: F01-1010).

calculated as 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.[8]

15 Keywords

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

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

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

8 Smith, S. P., and Metz, J., "Understanding the Correlation of Surface SIMS and TXRF Measurements of Surface Metal Contamination on Silicon 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.

SEMI MF1618-1104
PRACTICE FOR DETERMINATION OF UNIFORMITY OF THIN FILMS ON SILICON WAFERS

1 Purpose

1.1 The fabrication of semiconductor, dielectric, and metal thin films is a critical part of silicon integrated circuit production. The variation of film properties across the surface of a wafer can have significant impact on the further processing of the wafer and on the ultimate yield of acceptable chips from the wafer, as well as on their reliability.

1.2 The purpose of this practice is to promote commonality of approach to the analysis of uniformity among all parties needing to generate or assess such information, including manufacturers of the basic test instrumentation to be used.

1.3 This practice is intended for process control, research and development, and process equipment evaluation purposes. It is intended for the benefit of semiconductor device and equipment manufacturers alike so that acquisition, reduction, and communication of thin film data is consistent among various parties who may need to concur on interpretation of the results of a thin film fabrication-process step.

1.4 Measurement of the uniformity of one or more thin film properties such as thickness, sheet resistance, reflectivity, dielectric constant or index of refraction enables the monitoring of a critical aspect of the results of a given process step. This information can be used to determine the behavior of individual process steps; it can be used with similar information from earlier process steps to determine their interaction with respect to final product uniformity. Also, it can be used in conjunction with historical data from the same process step to determine loss of control of the piece of equipment or the process cycle being used with respect to producing product having a required level of uniformity. Further, it can be used to determine the adequacy of new or modified process cycles, materials or equipment for a given film deposition or film modification requirement.

1.4.1 It is common practice to monitor the value of a simple statistic, such as the standard deviation, that results from layer uniformity measurement data and to compare the current value of the statistic with historical values for the same layer formation process. An increase of the current value over historical values is taken as an indication of possible deterioration of the quality of the layer formation process. It is then common to convert the data into a contour or similar map of uniformity to aid in diagnosing changes in the process that caused the increase in standard deviation (or similar statistic). This practice does not treat the interpretation of the statistic resulting from data analysis, nor does it give procedures for converting the data to a uniformity map.

1.5 The non-uniformities of a film property on a given wafer are primarily systematic, not random, in their spatial shape or distribution and arise from spatially systematic variations in such process variables as temperature, gas flow, pressure, or electric field. As a result, the simple statistic standard deviation that is specified for analysis of data acquired with this practice will not generally have the normal interpretation for the standard deviation of a sample from a random population. It is a figure of merit for comparing data sets of a similar type, but it cannot be used for computing confidence or tolerance intervals.

2 Scope

2.1 This practice covers a set of site distribution patterns for measuring the uniformity of a property of a thin film on a silicon wafer, as well as simple procedures for analyzing and reporting the results of those measurements.

2.2 This practice is intended for use as a template for the evaluation of the uniformity of intrinsic film properties such as thickness or composition, and also film functional characteristics such as sheet resistance and reflectivity. The resulting information may be used to assess the uniformity of the film itself or of the layer formation process. This practice is not directly applicable to evaluating wafer-to-wafer or lot-to-lot variations.

2.3 This practice is intended for use with any thin film or layer type, or formation technique, for which basic measurement instrumentation and capability exists that, is appropriate to the film parameter of interest. This practice is intended for layer growth and deposition techniques such as epitaxy, implantation, thermal and

chemical vapor deposition (CVD) oxidation, and metallization, as well as for layer modification such as various means of layer etching.

2.4 This practice is intended for use with all silicon wafer sizes and types when measuring uniformity of film properties and characteristics. This practice describes measurement site patterns and determination of their spatial coordinates on the wafer, as well as the statistics to be used when reducing the measurement data to determine uniformity. For each of the sampling plans, the exact number of measurement sites is chosen based on the size of the wafer being used, the desired spatial resolution of the measurement instrument, and whether maximal, or somewhat lesser information density is desired. However, in all such choices, the pattern of measurement sites, the rules for selecting their coordinates on the wafer, and the statistical calculations of the results should remain consistent with the procedures of this practice.

2.5 This practice can be used with any measurement method, procedure or instrumentation that can measure the needed film property or characteristic with sufficient precision and spatial resolution to reveal the needed information on spatial non-uniformity of the film. This practice does not itself contain details on performing any specific measurement.

2.5.1 Not all types of measurements that may need to be used for evaluation of the uniformity of a thin film have formal procedural standards. SEMI MF374, SEMI MF576, SEMI MF1392, SEMI MF1393, and SEMI MF1529 give details of measurement procedures that may be applied to evaluating the uniformity of thin film properties.

2.5.2 This practice does not deal with acquisition or analysis of uniformity data where it is desired to take more than one measurement per specified spatial cell such as is commonly done for wafer site flatness measurements.

2.6 This practice makes no recommendations regarding the interpretation of the statistics that result from analysis of the data acquired with regard to the goodness or badness of given values of the test statistic, nor does it make recommendations regarding decisions about the process cycle or equipment used to produce the thin film that was measured.

2.7 The principles of this practice may be adapted to determine the uniformity of bulk silicon wafer properties such as interstitial oxygen content and resistivity, but depending on the desired property and the chosen measurement technique, depth-dependent variations may be misinterpreted as lateral variations.

NOTICE: This standard does not purport to address safety issues, 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 or other limitations prior to use.

3 Limitations

3.1 This practice is written for evaluation of planar or blanket films, but it may be applied to patterned films if the pattern size, shape, and distribution do not interfere with the spatial resolution of the selected measurement technique and the specified measurement site selection. If either of these interferences occur, the user may adapt the principles of the method to the needed application, but the interpretation of the results may change.

3.2 The principles of this practice may be adapted to other semiconductor wafers, such as gallium arsenide, but particular concerns with those other materials may not be addressed adequately in this practice.

3.3 Uniformity measurements from certain types of measurements may be misinterpreted if the user is not aware of the full nature of the basic measurement being made. For example, sheet resistance is a function both of the inherent resistivity of the film being measured and of its thickness value. Non-uniformity in sheet resistance values across the wafer may result from non-uniformity in resistivity (layer composition or structure) or layer thickness (deposition rate) alone, or it may result from simultaneous variations of both parameters.

3.4 Changes in test equipment performance, or changes in test procedure or conditions over time may detrimentally affect the ability to compare test results from this practice over time for a given film property or fabrication step. It is the responsibility of the user to ensure that the measurement system and process remains in sufficient control to allow time-wise comparison of uniformity results, if such comparisons are needed.

3.5 Sampling area or sampling spot-size may cause misinterpretation of the cause of thin film non-uniformity if the magnitude of the non-uniformity and its spatial scale, or rate of variation is not well matched to the sampling spot size and the selected distribution of measurement sites. While this should not be a serious concern for most modern film deposition processes, and process equipments, which are operating in control, the principles of this limitation are worth elaborating.

3.5.1 If the sampling area or the spot size of the test instrument is large compared to rates of film parameter change (gradients) that are important to identify, it must be recognized that such large sampling area instruments generate some form of spatial average response that

may understand macroscopic film non-uniformity or fail to respond to microscopic film non-uniformities or both.

3.5.2 If the sampling area or spot size is small, it is generally possible to quantify the full scale of macroscopic film non-uniformities. However, should spatial fine-scale systematic film variations be present, they may affect the individual measurements in an inconsistent manner unless the measurement sampling plan is tailored to the spatial size scale of the fine variations. Such tailoring of the sampling plan is generally incompatible with the requirements of this practice.

3.6 For the most meaningful interpretation of uniformity data, all sampling sites should represent equal wafer areas, and the available area of the wafer should be fully sampled. The existence of wafer flats causes a failure of the first requirement with all concentric circle sampling plans. The need of the semiconductor industry to establish as large a quality area as possible on wafers also causes a failure of the first requirement for the outermost circle of concentric circle sampling plans because of the need to measure right up to a very small edge exclusion value. The second requirement is not met near the perimeter of Cartesian sampling plans.

3.7 Ideally, measurements would be made at the specified sites in a random sequence so that instrument drift or changes in other environmental parameters that may affect measurement results would have a random correlation with measurement positions. It is normally not practical to acquire data in this fashion. Therefore, any instrumental or environmental change that may occur will have a correlation with the spatial ordering of the measurement sequence. While such changes are expected to have about the same effect on both concentric circle and Cartesian sampling plan measurements, providing the number of data points are about the same, they would nevertheless have different effects on two-dimensional contour maps that resulted from these two different types of sampling plans.

3.8 Individual test instruments and test methods that may be used to measure properties or characteristics of thin films are subject to various interferences that may affect measurement precision consistency, resolution, and accuracy. These may include such things as sensitivity to stray illumination, rf-fields, and variations in temperature. It is the responsibility of the user of this practice to consult instrument manuals and appropriate test methods in order to identify and control potential interferences with that instrument or method.

3.8.1 It is also the responsibility of the user to devise a test for the inherent precision of the measurement being made so that imprecision in the measurement is not misinterpreted as non-uniformity of the thin film being evaluated by this practice. This is particularly important for application of this practice to evaluating films from process steps that are capable of a very high degree of uniformity, for example, 1% across a wafer. Such tests may involve using known uniform or non-uniform test specimens whose spatial pattern of non-uniformity has been found to be very stable over extended periods of time.

4 Referenced Standards

4.1 *SEMI Standards*

SEMI M1 — Specifications for Polished Monocrystalline Silicon Wafers

SEMI M20 — Practice for Establishing a Wafer Coordinate System

SEMI MF81 — Test Method for Measuring Radial Resistivity Variation on Silicon Wafers

SEMI MF374 — Test Method for Sheet Resistance of Silicon Epitaxial, Diffused, Polysilicon, and Ion-Implanted Layers Using an In-Line Four-Point Probe with the Single-Configuration Procedure

SEMI MF576 — Test Method for Measurement of Insulator Thickness and Refractive Index on Silicon Substrates by Ellipsometry

SEMI MF673 — Test Methods for Measuring Resistivity of Semiconductor Slices or Sheet Resistance of Semiconductor Films with a Non-contact Eddy-Current Gage

SEMI MF1241 — Terminology of Silicon Technology

SEMI MF1392 — Test Method for Determining Net Carrier Density Profiles in Silicon Wafers by Capacitance-Voltage Measurements with a Mercury Probe

SEMI MF1393 — Test Method for Determining Net Carrier Density in Silicon Wafers by Miller Feedback Profiler Measurements with a Mercury Probe

SEMI MF1529 — Test Method for Sheet Resistance Uniformity Evaluation by In-line Four-point Probe with the Dual-configuration Procedure

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 Definitions of terms used in this practice may be found in SEMI M1 and SEMI MF1241.

6 Summary of Practice

6.1 Measurements are made at the sites specified in the chosen sampling plan using the appropriate instrumentation and measurement procedure for the film parameter of interest. Measures of the dispersion of the values are obtained by simple statistics specified for the sampling plans.

7 Apparatus

7.1 *Four-probe Sheet Resistance, Eddy-current, Mercury Probe CV, Spectroscopic Reflectometers, Ellipsometers, Interferometers, and Stylus Profilometers* — Typical apparatus chosen according to the type of material parameter being monitored. Others may be chosen according to need. The instrumentation should include such features as temperature monitoring and control, EMI shielding, shielding from illumination, etc. as is necessary for good practice of that type of measurement. In addition, all instrumentation must include the following:

7.1.1 Ability to center the wafer on the measurement stage to an accuracy of 0.5 mm or better,

7.1.2 Vacuum chuck, or similar fixture, to secure the wafer to the instrument stage during measurement,

7.1.3 Ability to locate the measurement points specified in the chosen sampling plan to an accuracy of 0.5 mm or better, and

7.1.4 Ability to store all measurement data to perform the required calculation of uniformity.

7.2 Capability of the instrumentation to perform one or more of the following auxiliary data presentations is highly recommended:

7.2.1 Generating a two-dimensional contour map of the acquired data,

7.2.2 Generating a histogram of the raw data values, and

7.2.3 Presenting the raw data as a time-series plot.

7.3 Capability to edit data and to blend or interpolate data in conjunction with two-dimensional mapping may be useful, but it should be done with caution.

8 Procedure

8.1 Calibrate the measurement system in accordance with the manufacturer's instructions or with the applicable test method.

8.2 Place the wafer on the instrument stage so as to locate the wafer center within 0.5 mm of the center of the stage. For the purposes of this procedure, the wafer center is considered to be defined by the intersection of any two diameters that do not intersect a wafer flat or orientation notch.

8.3 Select the sampling plan to be used from those listed in Appendix 1 and proceed to take measurements at all the specified locations. It may be necessary to enter the coordinates of the desired sampling plan into instrument software, or to work with the manufacturer of the equipment to modify its software if the sampling plans available in the instrument do not match the requirements of Appendix 1.

8.4 Take measurements at all locations specified for the selected sampling plan. Then quantify the uniformity from the acquired data using the calculations specified in Section 9.

9 Calculations

9.1 Calculate the mean, $\bar{x}$, and the standard deviation, s, of the N measurement values, x_i, as follows:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \text{ , and} \tag{1}$$

$$s = \left(\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2\right)^{1/2} \tag{2}$$

9.2 Examine the data. If agreed upon between parties to the test, reject values that are away from the mean by more than three times the standard deviation calculated in Section 9.1. Recalculate the mean and standard deviation using Equations 1 and 2, where N is now the reduced number of data points.

NOTE 1: It is generally advisable, through use of a time series plot of the original data, or similar means, to inspect the data just rejected for determination of measurement site location and relation to adjacent measurement values.

NOTE 2: The calculation for standard deviation may be made regardless of any systematic behavior of the underlying distribution of measured values. However, when there is a systematic spatial behavior to the measured values, the standard deviation may not be used to estimate confidence intervals or tolerance limits.

9.3 Calculate the following two statistics from the complete data set or from the reduced data set if certain measurements were rejected in Section 9.2. These two statistics represent the range and the distribution of data about the mean. The use of only one of these statistics is at the discretion of the interested parties.

9.3.1 High-Low Variation, *HLV*, in percent:

$$HLV(\%) = \frac{x_{\max} - x_{\min}}{x_{\max} + x_{\min}} \times 200 \tag{3}$$

9.3.2 Standard Deviation Uniformity, *SUP*, in percent:

$$SUP(\%) = \frac{s}{\bar{x}} \times 100 \qquad (4)$$

10 Report

10.1 Report the following information when describing the uniformity of a specific thin film parameter across the surface of a wafer:

10.1.1 Wafer identification and diameter,

10.1.2 Operator and date,

10.1.3 Substrate type (orientation and doping, if appropriate),

10.1.4 Generic film type, and reactor, run or process information, as appropriate,

10.1.5 Film parameter measured and assumed material constants used for analysis,

10.1.6 Sampling plan used,

10.1.7 Test method used by designation, if available, or by brief description if no standard procedure is available,

10.1.8 Test instrument manufacturer, model, options,

10.1.9 Total number of points measured; number of points within 3-sigma; number of points used to calculate *HLV* and *SUP*,

10.1.10 Calculated *HLV(%)*, *SUP(%)*, mean value ($\bar{x}$), and sample standard deviation, *s*.

10.2 Two-dimensional contour plot, data histogram, or time series plot of measurement values may be included if agreed upon between the parties to the test.

10.3 For a single-diameter sampling plan, also report the angle between the diameter measured and the fiducial axis.

11 Precision and Bias

11.1 *Precision* — The precision with which wafer uniformity can be measured is governed by the precision of the individual test method being used.

11.2 *Bias* — The bias associated with the wafer uniformity measurements is also governed by the bias of the individual test method being used.

11.3 The Precision and Bias sections of the test method being used should be consulted.

NOTE 3: The Appendix[1] of SEMI MF81 gives, for the case of sparse site sampling plans, an example of the propagation of error from the basic measurement technique to the determination of variation of material properties using that technique.

11.4 The standard deviation and range calculations that are specified in Section 9 are descriptive statistics or figures of merit for describing the uniformity of the thin film wafer in a simple and consistent manner, but they are generally not appropriate for determining the precision of the measurements.

12 Keywords

12.1 dielectric layers; epitaxial layers; ion implant; metal films; sampling plans; semiconductor; silicon; thin films; uniformity

---

1 This non-mandatory section will be called Related Information after this standard has been reformatted and adopted through the SEMI Standards process.

APPENDIX 1
SAMPLING PLANS TO BE USED FOR WAFER UNIFORMITY DETERMINATION

NOTICE: The material in this appendix is an official part of SEMI MF1618 and was approved by full letter ballot procedures.

A1-1 Introduction

A1-1.1 For all plans, measurements are made within a circular area defined by the radius, R_o, between the center of the wafer and the circle on which the centers of the outermost measurement sites lie. Determine this radius by either of the following methods:

A1-1.1.1 *Method A* — In this method, the outermost edges of the measurement spots on the outermost radius are tangent to the boundary of the fixed quality area (FQA) as defined in SEMI M1:

$$R_o = \left(\frac{D}{2} - (EE + \frac{d}{2}) \right) \qquad \text{(A1-1)}$$

where:

R_o = radius of the outermost measurement circle (see Figure A1-1),

D = nominal diameter of the wafer, for example, 100, 150, 200, or 300 mm,

EE = nominal wafer edge exclusion, which determines the FQA, and

d = known or estimated diameter of the measurement spot for the test instrument being used (Note 1).

NOTE 1: The exact diameter of the measurement spot may not be known for many types of measurements. Estimate the diameter as 1.5 times the probe spacing for a four-point probe, transducer radius for an eddy-current instrument, and apparent beam spot radius for optical measurements if no other information is available.

A1-1.1.2 *Method B* — In this method, the centers of the measurement spots on the outermost radius are on the boundary of the fixed quality area (FQA) as defined in SEMI M1:

$$R_o = \left(\frac{D}{2} \right) - EE \qquad \text{(A1-2)}$$

where the symbols are defined following Equation A1-1.

A1-2 Selection of Method

A1-2.1 Neither of these methods is "better" than the other; rather, there are tradeoffs.

A1-2.2 The location of every point in a multipoint measurement pattern depends on the method chosen to define the position of the outermost measurement sites. Therefore, there may be differences between the two methods for reported individual and statistical values.

A1-2.3 Data for a measurement site are usually reported at the location corresponding with the center of the measurement spot.

A1-2.4 Data from each measurement on the outermost ring in Method A are not affected by the film properties in the edge exclusion annulus outside the FQA. However, in this case, data are not reported for locations closer to the boundary of the FQA than the measurement spot radius.

A1-2.5 Conversely, data from each measurement on the outermost ring with Method B include contributions from film properties both inside and outside the FQA. In this case, measurement data is reported for locations up to the boundary of the FQA, but establishing the significance of including data influenced by film properties outside the FQA is outside the scope of this practice.

NOTE 2: Measurements obtained using a probe whose effective measurement area extends beyond the edge of the film inaccurately represent actual film properties.
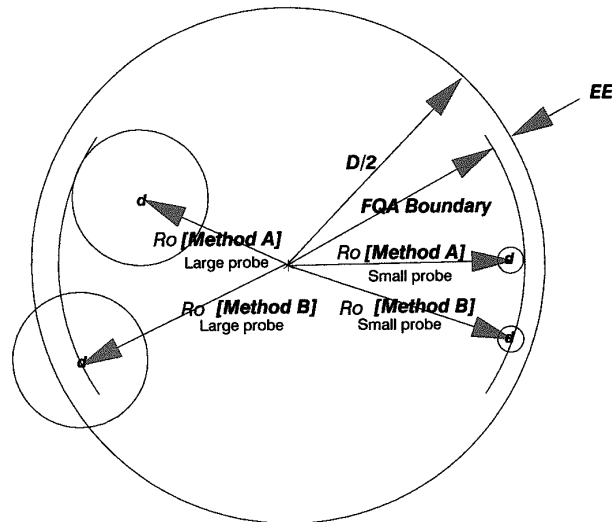

Figure A1-1
FQA Boundary and Outermost Ring Radii, R_o, for Methods A and B

A1-3 Concentric Circle Plans[2]

A1-3.1 The concentric circle plans are designed so that each measurement location samples approximately an equal area of the specimen surface. Because these are circular plans on a circular wafer, ideally they give equal representation to all portions of the wafer's surface. This approximation to equal-area sampling breaks down for the outermost circle if the size of the edge exclusion is less then half the radial separation between the inner circles for the spacing being used. In this case, the measurements on the outer circle represent a smaller area of silicon than do the measurements on the inner circles. Moreover, if the actual sampling area of the measurement being used is larger than the value estimated in Section A1-1.1.1, measurements on the outer circle may be partially influenced by thin film properties in the excluded region even though the resulting values are attributed to the fixed quality area of the film.

A1-3.2 The concentric circle sampling plans utilize a measurement at the wafer center and points on a number of concentric circles designated 1, 2, 3, ... n, the number of circles being chosen by the user according to wafer diameter, estimated sampling area for the measurement being made, and the amount of information desired about the uniformity of the thin film.

A1-3.2.1 On each circle, the measurements are separated by equal angular intervals. Eight measurements are made on the first circle, 16 are made on the second circle, etc. In general, the number of measurements is eight times the circle number. For the first circle, measurements are separated by rotations of 45°, for the second circle, by 22.5°, and so forth, regardless of the radial value of the measurement or the wafer diameter.

A1-3.2.2 The radial values for the concentric circles are determined as follows. Inspect Table A1-1 for the number of total measurements that are made as a function of the number of circles used and decide on the number of circles according to the amount of information needed for the film uniformity and the time required for the test instrument to take that many measurements. Call the chosen number of circles, N_C. Divide the value of the outermost radius, R_o, determined in Section A1-1.1, by N_C. This gives the radial increment between the circles. The center of the measurement tool or measurement spot is to be placed at the location given by this radial increment value.

---

2 Keenan, W. A., Johnson, W. M., and Smith, A. K., "Production Monitoring of 200 mm Wafer Processing" in *Emerging Semiconductor Technology*, ASTM International STP 960, edited by D. C. Gupta and P. H. Langer (ASTM International, West Conshohocken, PA, 1986) pp. 598–614.

Figure A1-2 illustrates measurement locations for three-circle and four-circle sampling plans.

NOTE 3: If the incursion of the orientation flat(s) precludes taking valid measurements near the flat in conjunction with the chosen edge exclusion, the parties to the test may choose to exclude specified measurement locations if the test instrument permits or to replace specified sites with sites at a distance from the flat that is equal to the distance specified with respect to the circular perimeter of the wafer. It must be remembered, however, that either such choice may have an adverse impact on the interpretation of any two-dimensional contour map.

Table A1-1 Number of Measurement Sites for Various Numbers of Concentric Circles

Number of circles	3	4	5	6	7	8
Number of sites	49	81	121	169	225	289

A1-3.2.3 For consistency, place the wafer on the instrument stage with the primary flat, or notch, facing the operator. If another convention becomes necessary, so note it on the report. Measurements are made starting at the center of the wafer then proceeding around the first, then the second, then the third circle, and so forth. For all circles, make sure that the first measurement is made at the same angular orientation; the positive x-axis or the positive y-axis, as defined in the wafer coordinate system specified in SEMI M20, is recommended. The choice should have no bearing on the data or its analysis. However, if data is to be presented as a time-series plot, note on the plot the position of the first point on each circle as well as whether the measurements proceed in a clockwise or counterclockwise fashion on the wafer surface.
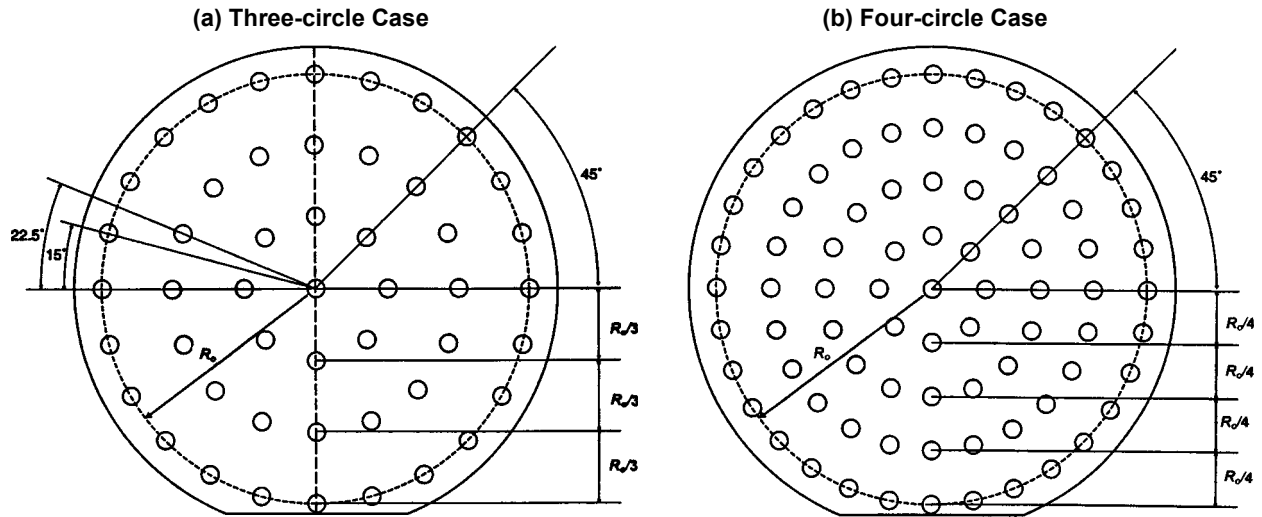
A1-3.3 Calculate the uniformity based on the difference between the maximum and minimum measured values, *HLV(%)*, and on the standard deviation as a percent of the mean of all measurements, *SUP(%)* as detailed in Section 9.3.

A1-4 Cartesian Sampling Plans

A1-4.1 Cartesian sampling plans sample equal areas in the interior of the wafer surface, but fail to sample portions of the wafer near its perimeter. They may not provide sufficient information about the outermost portion of the fixed quality area for a given application. See Figure A1-3 for an illustration in the case of a 37-point Cartesian sampling plan.
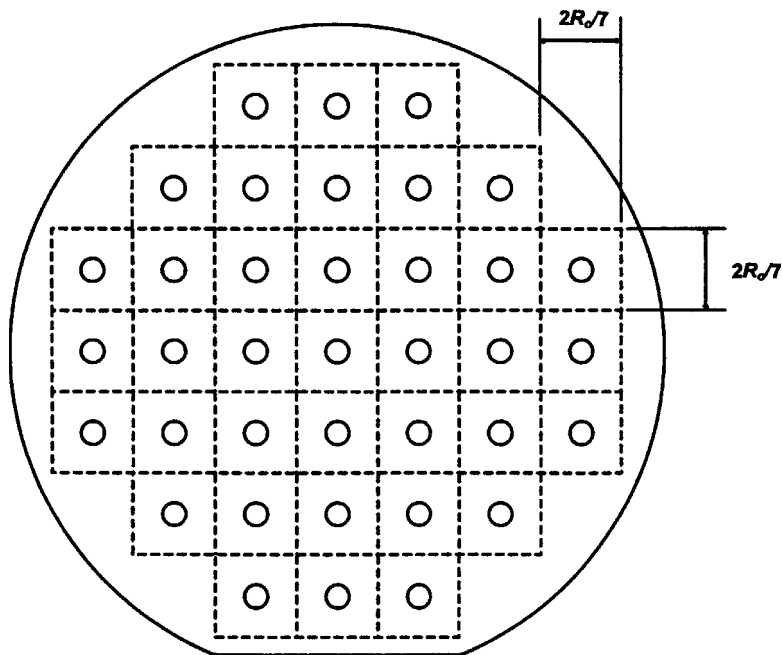
A1-4.2 These plans have a grid of equal-sized cells, equally spaced about the center of the wafer. A measurement is made in the center of each cell. The number of rows and columns in the grid, always an odd number, is chosen according to wafer diameter, estimated sampling area for the measurement being

made, and the amount of information desired about the uniformity of the thin film. The square cells in this plan are not necessarily the shape or size of the sampling area for the measurement being used. In general, make sure that the sampling area for the measurement is smaller than the dimensions of the square.

(a) Three-circle Case   **(b) Four-circle Case**

NOTE: The radius R_o is given by Equation A1-1 for Method A and by Equation A1-2 for Method B.

Figure A1-2
Illustrations of Concentric Circle Sampling Plans

NOTE: The radius R_o as discussed in A1-1.1 is not shown in this figure.

Figure A1-3
Illustration of the Cartesian Measurement Site Plan for the Case of Seven Rows by Seven Columns

Table A1-2 Approximate Number of Measurement Sites for Various Numbers of Rows and Columns in a Cartesian Sampling Plan

Number of rows and columns	7	9	11	13	15	17
Number of sites	37	69	97	137	177	225

A1-4.3 The size of the cells, and the separation of the measurement sites along the *x*- and *y*-axes, is determined by the number of rows and columns into which the wafer surface is partitioned. Use Table A1-2 as a guide to the approximate number of measurement sites for various numbers of rows and columns of cells. To calculate the dimensions of the square cells, divide the outermost radius, R_o, determined in Section A1.1, by N, the desired number of rows and columns. The exact number of sites that will be measured is governed by the number of cells near the wafer perimeter that need to be excluded because the center of the cell, that is, the center of the measurement spot, does not fall within the radius R_o.

A1-4.4 Use test instrument software to establish the coordinates of the center of all cells as determined from the ratio R_o/N_C, calculated in Section A1-4.3. Disallow measurement sites near the wafer perimeter such that the radial distance to the center of the cell, that is, the center of the measurement spot, is larger than R_o. This follows the same rationale for allowed measurement sites as is used with the concentric circle plans.

A1-4.5 Take measurements at all sites allowed in accordance with Table A1-2. The measurement sequence, whether starting from the center point and moving outward or starting from one edge a row or column at a time, is to be decided by the parties to the test.
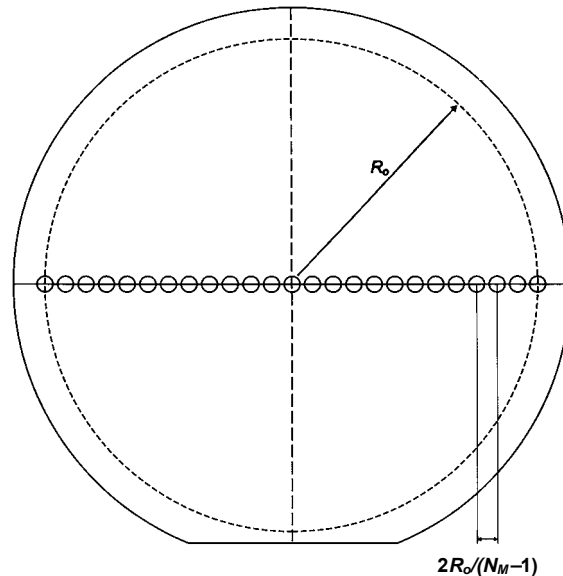
A1-4.6 Calculate the uniformity based on the difference between the maximum and minimum measured values, *HLV(%)*, and on the standard deviation as a percent of the mean of all measurements, *SUP(%)*, as detailed in Section 9.3.

A1-5 Single-Diameter Sampling Plan

A1-5.1 This plan uses a very high density of measurements along a diameter and includes a measurement at the wafer center. It is shown schematically in Figure A1-4 for the diameter being parallel to a major wafer flat. However, in the case of notched wafers, the notch would replace the flat in the figure. It is also possible, by agreement of the parties to the test, to make the measurements along a diameter at

a specified angle with respect to the fiducial axis as long as such an angle is then stated in the report.

A1-5.2 Choose a value, N_M, for the number of measurements, where N_M is at least 25. The separation between measurement sites is given by $2R_o/(N_M - 1)$, where R_o is determined as in Section A1-1.1.

NOTE: The radius R_o is given by Equation A1-1 for Method A and by Equation A1-2 for Method B.

Figure A1-4
Illustration of Single-Diameter, High-Density Measurement Site Plan

A1-5.2.2 Compare the site separation, $2R_o/(N_M - 1)$, with the estimated measurement sampling area or spot size. If the interval is smaller than this value, little additional information may be obtained by choosing so large a value for N_M; it may be appropriate to reduce N_M so that the new calculated site separation is equal to or greater than the measurement sampling area.

A1-5.3 Establish the coordinates for all measurement sites using the site interval value just calculated and the wafer center as the reference point. Take measurements at all sites.

A1-5.4 Calculate the uniformity based on the difference between the maximum and minimum measured values, *HLV(%)*, and on the standard deviation as a percent of the mean of all measurements, *SUP(%)*, as detailed in Section 9.3.

NOTICE: SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature, respecting any materials or equipment mentioned herein. These standards are subject to change without notice.

By publication of this standard, Semiconductor Equipment and Materials International (SEMI) takes no position respecting the validity of any patent rights or copyrights asserted in connection with any items mentioned in this standard. Users of this standard are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights are entirely their own responsibility.

SEMI MF1630-0704
TEST METHOD FOR LOW TEMPERATURE FT-IR ANALYSIS OF SINGLE CRYSTAL SILICON FOR III-V IMPURITIES

1 Purpose

1.1 Electronic grade polysilicon producers and users rely on LTFT-IR spectroscopy to evaluate polysilicon for quality assurance and research purposes.

1.2 LTFT-IR spectroscopy identifies and quantitates boron, phosphorus, aluminum, arsenic, indium, antimony, and gallium.

1.3 LTFT-IR spectroscopy can be applied to FZ, CZ, or other single crystal silicon (either doped or undoped) up to the concentration limits given in Section 2.2.

1.4 The measurement of carbon in silicon at low temperature can be accomplished concurrently in accordance with SEMI MF1391. The carbon can be measured at lower concentrations at <15 K than is possible at room temperature because the two-phonon band transmission is increased by a factor of two allowing greater throughput to the detector that results in an increased signal to noise ratio. Also the carbon adsorption band narrows from a FWHM of 5 to 6 cm^{-1} to a FWHM of 2.5 to 3.0 cm^{-1} at these low temperatures.

2 Scope

2.1 This test method covers the determination of electrically active boron, phosphorus, arsenic, aluminum, antimony, and gallium concentration in single crystal silicon.

2.2 This test method can be used for silicon in which the impurity/dopant concentrations are between 0.01 ppba and 5.0 ppba for each of the electrically active elements.

2.3 The concentration for each impurity/dopant can be obtained by application of Beer's Law. Calibration factors are given for each element.

NOTICE: This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health guides and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 The sample specimen must be colder than 15 K for measurement of electrically active species. If the sample specimen is mounted on a cold finger, care must be taken to obtain good contact between the sample specimen and the cold finger for efficient heat transfer. The oxygen absorption lines at 1136 cm^{-1} and 1128 cm^{-1} are sensitive to temperature and can be used to determine the specimen temperature.[1] When the sample specimen is less than 15 K the net absorbance at 1136 cm^{-1} is three times larger than the net absorbance at 1128 cm^{-1}. A ratio of greater than three is obtained for temperatures below 15 K.

3.2 Without sufficient incident white light the compensated donors and acceptors will not absorb. Therefore, the white light intensity must be great enough to completely neutralize all the compensated donors and acceptors. The intensity of the white light necessary must be determined for each system. The user should increase the intensity of the white light until further increase in intensity no longer affects the area/height of the electrically active impurity/dopant peaks.

3.3 Water vapor absorption interferes with the measurement of several peaks. Consequently, the background spectrum should be collected at least daily. The entire light path, including the sample chamber, must be purged to remove moisture. Special care should be taken whenever a sample specimen is changed so that the moisture level in the sample chamber or elsewhere in the light path is not affected.

3.4 Oxygen level in Czochralski silicon can be high enough to exhibit thermal donor absorption lines. These lines fall between 400 cm^{-1} and 550 cm^{-1} and can interfere with aluminum (473 cm^{-1}), gallium (548 cm^{-1}), and occasionally arsenic (382 cm^{-1}). Thermal donors can be removed by annealing the sample specimen.

---

1 Rome, J. J., "Calibration Relationships for Optically Measuring the Concentrations of Boron, Gallium and Indium in Silicon," Thesis, School of Engineering, Air Force Institute of Technology (1982), pp. 46–47.

3.5 Multiple internal reflections can produce a secondary interferogram and baseline oscillations. Changing the sample specimen thickness, the surface preparation, or the resolution can eliminate the secondary interferogram and the baseline oscillation.

3.6 High antimony levels interfere with the 320 cm^{-1} boron absorption line. Antimony's strongest absorption line is 293 cm^{-1}, but a secondary absorption line occurs at 320 cm^{-1}.

4 Referenced Standards

4.1 *SEMI Standards*

SEMI MF723 — Practice for Conversion Between Resistivity and Dopant Density for Boron-Doped, Phosphorus-Doped, and Arsenic-Doped Silicon

SEMI MF1241 — Terminology of Semiconductor Technology

SEMI MF1391 — Test Method for Substitutional Atomic Carbon Content of Silicon by Infrared Absorption

SEMI MF1723 — Practice for Evaluation of Polycrystalline Silicon Rods by Float-Zone Crystal Growth and Spectroscopy

4.2 *ASTM Standards*

E 131 — Terminology Relating to Molecular Spectroscopy[2]

E 168 Practices for General Techniques of Infrared Quantitative Analysis[2]

E 177 — Practices for Use of the Terms Precision and Bias in ASTM Test Methods[3]

E 275 — Practice for Describing and Measuring the Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers[2]

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 General definitions for terms related to infrared absorption spectroscopy are found in ASTM Terminology E 131.

5.2 Definitions for terms related to silicon materials technology are found in SEMI MF1241.

5.3 *Abbreviations and Acronyms*

5.3.1 *FT-IR* — Fourier transform infrared (spectrometer).

5.3.2 *FWHM* — full width of an absorption peak expressed in cm^{-1} at half its absorbance magnitude as measured from the baseline.

5.3.3 *LTFT-IR* — low temperature, Fourier transform infrared (spectrometer).

5.4 *Definitions*

5.4.1 *background spectrum*, *n* — in FT-IR instruments, the single-beam spectrum obtained without a specimen in the infrared light path that is usually obtained with only nitrogen, dry air, or a vacuum in the beam.

5.4.2 *baseline*, *n* — a straight line interpolation between points on either side of the absorption peak of the absorbance spectrum.

5.4.3 *electrically active elements*, *n* — dopants or impurities in silicon that are members of either Group III (boron, aluminum, gallium, and indium) or Group V (phosphorus, arsenic, antimony, and bismuth) of the periodic table.

5.4.4 *sample spectrum*, *n* — the ratio of a spectrum obtained with the test specimen in the IR beam to a background spectrum.

6 Summary of Test Method

6.1 A sample specimen of single crystal silicon is cooled to less than 15 K. Under these conditions the number of free carriers becomes negligibly small and the IR spectrum of the sample exhibits a series of absorption bands that are characteristic for each shallow impurity species.[4]

6.2 The sample specimen is illuminated with an incident white light source to flood the silicon with photons of greater energy than the silicon band gap to allow neutralization of compensated impurities.[5]

6.3 An infrared beam is directed through the sample specimen and a transmitted spectrum is collected. The spectrum is ratioed to the background spectrum and then converted to an absorbance spectrum.

6.4 Baselines are constructed at one of the characteristic absorption bands for each impurity/dopant to be measured.

---

2 *Annual Book of ASTM Standards*, Vol 03.06, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Telephone: 610-832-9500, Fax: 610-832-9555, Website: www.astm.org
3 *Annual Book of ASTM Standards*, Vol 14.02.

4 Kolbesen, B. O., "Simultaneous Determination of the Total Content of Boron and Phosphorus in High-Resistivity Silicon by IR Spectroscopy at Low Temperature," *Appl. Phys . Lett.* 27, 353–355 (1975).
5 Baber, S. C., "Net and Total Shallow Impurity Analysis of Silicon by Low Temperature Fourier Transform Infrared Spectroscopy," *Thin Solid Films* 72, 201–210 (1980).

6.5 The areas of the absorption bands are measured.

6.6 Concentrations of each impurity/dopant are calculated in accordance with Bouguer-Beer's Law with factors given in this test method.

7 Apparatus and Materials

7.1 *Cryostat* — To maintain the sample specimen temperature below 15 K. This cryostat may be liquid helium immersion, exchange gas, or closed cycle refrigeration.

7.2 *Sample Specimen Holder* — Constructed of high heat conductivity metal with an aperture(s) to block any of the infrared beam except that passing through the sample.

NOTE 1: The procedure of Section 11 is based on the assumption that the cryostat can accommodate and utilizes a multi-sample holder.
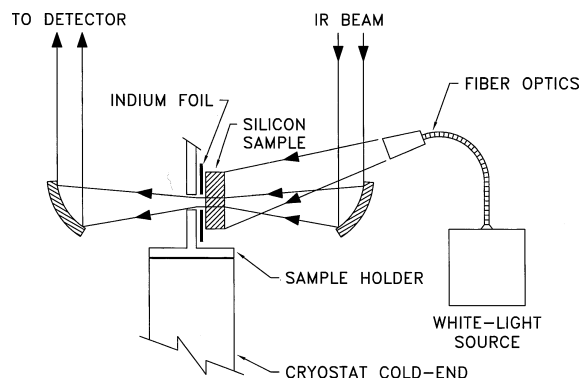
7.3 *White-light Source* — As shown in Figure 1.

Figure 1
Sample Holder and Optics Suitable for Illumination with White Light via Fiber Optics

7.4 *Fourier Transform Infrared Spectrometer (FT-IR)* — Must be equipped with suitable optics and detector for use in the region from 250 cm^{-1} to 1300 cm^{-1}.

7.4.1 The spectrometer shall be capable of at least 1.0 cm^{-1} resolution. The resolution shall be sufficient so that after zero-filling, apodization, and Fourier transformation the phosphorus adsorption band at 315.9 cm^{-1} has a FWHM not to exceed 1.1 cm^{-1}.

7.4.2 The detector shall be sufficiently sensitive to provide a reasonable signal to noise response in the desired spectral region. A room temperature DTGS with a CsI window suffices for the higher concentrations of elements in this test method. However, a zinc-doped germanium Ge:Zn detector operated at 4.4 to 10.0 K is preferred to give a signal-to-noise ratio sufficient to properly determine the

elements at the lower concentrations and for improved precision.

7.5 *Calcium Fluoride Crystal (CaF$_2$)* — Cut to nominal thickness of 5 mm.

8 Sample Preparation

8.1 If the samples are from polysilicon, they must first be converted to single crystal in accordance with SEMI MF1723 or other established means.

8.2 Sample specimen shall be cut and polished to fit the sample specimen holder. The surface may be mechanically or chemically polished. Each sample specimen shall have a thickness variation of less than 1% of overall thickness.

8.3 For measurement of electrically active impurities, the sample specimen thickness should be as follows:

8.3.1 For high purity silicon (>2000 Ω·cm): 3 to 5 mm to allow for lower detection limits.

8.3.2 Between 5 and 20 mm in cases where impurity levels to be measured are below 0.01 ppba.

8.3.3 For heavily doped silicon (<10 Ω·cm): 1 to 2 mm to allow greater transmission of the infrared radiation.

9 Reference Specimens

9.1 One or more silicon samples that contain impurities in the range of the samples to be tested shall be classified as reference specimens. These reference specimens should be analyzed repeatedly and periodically according to this test method. Compare the results obtained to previous data to establish that the measurement process is in control.

10 Testing of the Instrument

10.1 Establish FT-IR instrument stability by checking the 100% transmittance line.

10.1.1 Collect and store two background spectra sequentially through an open aperture of the cryostat specimen holder.

10.1.2 Ratio these two spectrum to obtain a transmittance spectrum.

10.1.3 Examine the spectrum from 1200 cm^{-1} to 250 cm^{-1}. The spectrum should be $100 \pm 0.5\% \, T$ over this range. Proceed only if the spectrum is $100 \pm 5\%$ over this range, otherwise correct any instrumental instability.

10.2 Check for detector linearity.[6]

10.2.1 Examine one of the two single-beam (unratioed) spectra obtained in Section 10.1.1 for nonzero response at wavenumbers where the detector is known to have zero response (below 200 cm^{-1} for the zinc doped germanium detector with a CsI window). The observed response in this region should be less than 1.0% of the maximum response over the 1200 to 250 cm^{-1} region. If not, take corrective action before proceeding.

10.2.2 Alternatively, collect a spectrum with a CaF_2 crystal wafer, 5 mm-thick, in the IR beam. Ratio this spectrum relative to one of the background spectrum obtained in Section 10.1.1 to obtain a transmittance spectrum. CaF_2 is totally opaque below 800 cm^{-1}. The spectrum must give $0.0 \pm 0.5\%$ transmittance from 800 to 250 cm^{-1}. If not, take corrective action before proceeding.

11 Procedure

11.1 Measure the thicknesses to ± 0.02 mm and load all the sample specimens to be examined onto the sample specimen holder leaving at least one open slot. Include a reference specimen to serve as an audit to ensure that the entire instrument is performing correctly.

11.2 Mount them in the cryostat and cool the samples to less than 15 K.

11.3 Set instrumental parameters to give a resolution of 1.0 cm^{-1} or better.

11.4 Select the reference specimen as the first sample to be measured.

11.5 Collect 1000 scans of an empty sample chamber slot and use this as the background spectrum.

11.6 Move the sample specimen into position.

11.7 Turn on the incident white-light source and ensure that the sample specimen is fully illuminated with white light and properly aligned relative to the IR beam (see Figure 1).

11.8 Collect a minimum of 300 scans of the sample.

11.9 Zero-fill, apodize, and transform the interferogram into a spectrum and then ratio it to the background spectrum.

11.10 Covert to an absorbance spectrum and use as the sample specimen spectrum.

11.11 Store this spectrum and subsequent ones for further manipulation and measurement of the peak areas.

11.12 Repeat Sections 11.5 through 11.11 for each sample specimen.

12 Data Reduction

12.1 This test procedure requires the measurement of the areas of the absorption bands before calculation of the concentration of each element. The absorption bands are very sharp, especially for the Group V elements, and therefore peak height measurements are difficult to reproduce from instrument to instrument. Use of peak areas greatly reduces this variability.

12.1.1 Establish baselines for each peak before measurement of the area. Use only the area above the established baseline in the calculations. Several algorithms are available on various commercial FT-IR instruments to obtain the desired baseline corrected areas. The following is one suggested method:

12.1.1.1 Retrieve the sample absorbance spectrum from the computer storage disk. With the wavenumber expand commands available, zoom in on the region of the absorption band(s) of interest. Expand until this region is only slightly larger than the baseline limit regions given in Table 1.

12.1.1.2 Employ the interactive baseline correction routine to bring the spectral baseline to coincide with the 0.0 absorbance line. Refer to Table 1 for the upper and lower wavenumber regions for guidance in adjusting the baseline. Expand in the absorbance scale as necessary to improve the observation of the noise and fine features of the spectrum in order to provide the best placement of the baseline. Apply only linear corrections with the fit of the straight line through the points on both sides of the absorption peak(s). Note that the peaks for boron and phosphorus are very close together and thus only one baseline is obtained surrounding both peaks. Figures 2 and 3 show spectra before and after, respectively, baseline correction for boron and phosphorus spectral region.

12.1.2 Measure the area for the absorption peak between the upper and lower wavenumbers given in Table 1 for the integration limits. Most computer algorithms handle this nicely. However, disable the automatic zeroing of the baseline at the integration limits. If not disabled, the integration would not represent the baseline as established in Section 12.1.1 and may result in errors.

12.1.3 Repeat Sections 12.1.1 and 12.1.2 for each component desired for each specimen measured.

---

6 Chase, D. B., "Nonlinear Detector Response in FT-IR," *Applied Spectroscopy* **38**(4), 491–494 (1984).

Table 1 Peak Location, Baseline and Integration Limits, and Calibration Factors

Element	Peak cm^{-1}	Baseline Limits		Integration Limits		Factor[A] $f(mm\text{-}cm)$
		Upper	Lower	Upper	Lower	
Aluminum (Al)	473.2	479	467	475.2	471.2	32.7
Antimony (Sb)	293.6	296	289	295.1	292.1	10.6
Arsenic (As)	382.0	385	379	383.5	380.5	8.96
Boron (B)	319.6	323	313	321.5	318.0	9.02
Gallium (Ga)	548.0	552	544	549.5	546.5	42.4
Indium (In)	1175.9	1181	1169	1177.4	1174.4	244.0
Phosphorus (P)	316.0	323	313	317.5	314.5	4.93

[A] The factors given here do not all have the same degree of certainty. The factors for boron, phosphorus, and arsenic are believed to be correct to better than ± 10%. The other factors should be considered approximations and used for estimations only. A discussion of the origin of these factors is given in Related Information 1.

13 Calculation

13.1 Calculate the concentration of each of the electrically active impurity/dopant in each specimen measured according to the following equation:

$$C_{ij} = \frac{I_{ij}}{t_j} f_i \qquad (1)$$

where:

C_{ij} = concentration of impurity/dopant element i, ppba, in sample specimen j,
I_{ij} = integrated area of component i,
t_j = thickness of sample specimen j, mm, and
f_i = calibration factor for component i, mm-cm.

13.2 The concentration may be expressed as density in units of atoms/cm^3 as follows:

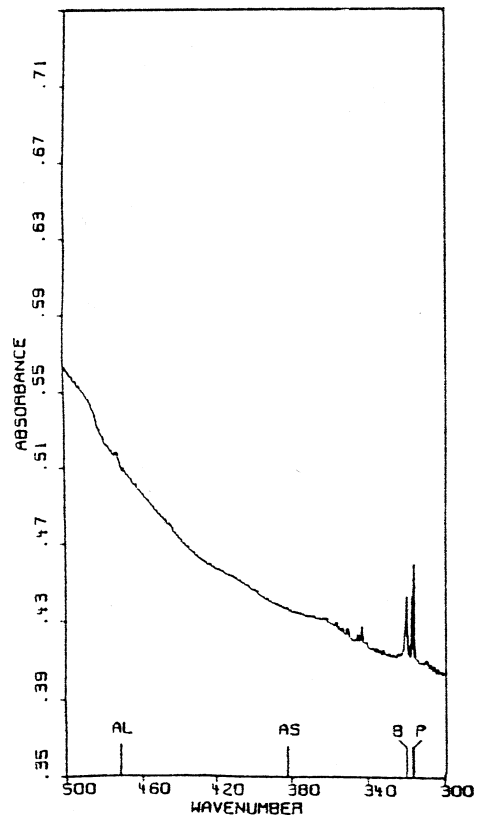$$D_{ij} = 5.0 \times 10^{13} C_{ij} \qquad (2)$$

Figure 2
Typical Infrared Spectrum in the Spectral Region for Aluminum, Arsenic, Boron, and Phosphorus at 11 K
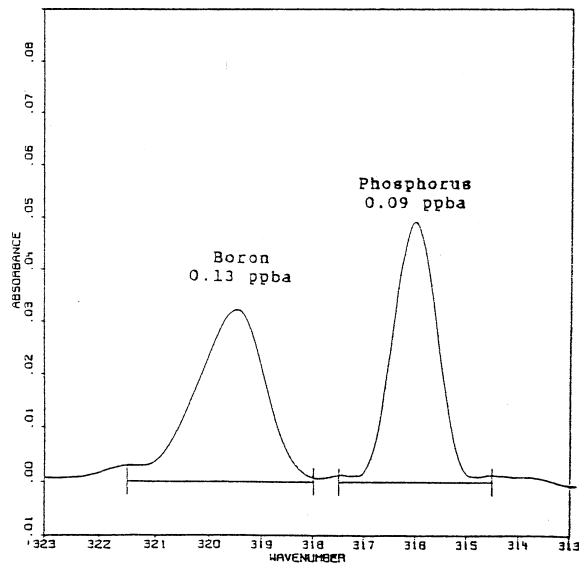
Figure 3
Boron and Phosphorus Region Expanded and
Baseline Corrected

14 Report

14.1 Report the following information:

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

14.1.2 Identification of specimens,

14.1.3 The results of the audit reference specimen on a control chart or other suitable form,

14.2 For each sample specimen report the following information:

14.2.1 The concentration of each impurity/dopant or the detection limit if no peaks can be identified,

14.2.2 Sample thickness,

14.2.3 The FWHM for each absorption peak,

14.2.4 The apodization function used, and

14.2.5 The amount of zero-fills and resulting number of data points/cm^{-1}.

15 Precision

15.1 A within-laboratory precision was determined by measurement of boron and phosphorus in a reference specimen by multiple operators over a period of one year. The relative precision was determined to be 8.5% and 9.7% for boron and phosphorus, respectively, at nominal concentrations of 0.095 and 0.072 ppba.

16 Bias

16.1 The bias of this test method is not known but believed to be within ± 10% of an accepted reference value.

17 Keywords

17.1 analysis of silicon; determination of dopants; determination of impurities; electrically active impurities; Fourier transform infrared; impurities; silicon.

RELATED INFORMATION 1
DERIVATION OF FACTORS USED IN CALCULATING CONCENTRATIONS AND DENSITIES OF ELEMENTS IN SILICON

NOTICE: This related information is not an official part of SEMI MF1630. It was developed as non-mandatory information in ASTM during the initial development of the document in 1994-5. This related information was approved for publication by SEMI by full letter ballot procedures on March 14, 2004.

R1-1 The factors shown in Table 1 resulted from several years of corrections and modifications but are ultimately based on resistivity measurements on silicon samples. The dopant density, or the concentration of impurities for this test method, is directly obtained from the conversion Tables found in SEMI MF723.

R1-2 Baber's[5] calibration factors published in 1980, were the starting point for the current factors. Corrections or modifications, or both, to his published data follow in this discussion.

R1-2.1 Baber's LTFT-IR study utilized the conversion relations reported by Irvin[7] in 1962, relating resistivity and impurity concentrations. Currently, the conversion tables given in SEMI MF723 are believed to be more reliable. Corrections to Baber's factors were made to reflect these new conversion tables.

R1-2.2 The factors of Baber relate peak heights of the absorption bands to concentrations. Peak heights are extremely sensitive to several FT-IR parameters. The phosphorus band at 316.0 cm^{-1} and the arsenic band at 382.0 cm^{-1} are very narrow, about 0.25 cm^{-1}, and thus the peak heights of these bands vary greatly with nominal resolution, type of apodization, degree of zero-filling, and mechanical strain on the sample. The boron absorption at 319.6 cm^{-1} band used in this test method is actually a composite of four separate boron absorption bands. The variability of the measurement of the absorption bands is reduced considerably when peak areas are used instead of peak heights. The use of peak areas is common in the field and their use is specified in this test method.

R1-2.3 Further minor modifications have been made over the in the period from about 1985 to about 1995 in several laboratories that use LTFT-IR spectrometers for determination of electrically active impurities.

R1-2.3.1 Studies with and without the white light on the silicon samples, covering a wide range of concentrations, are valuable as tools to check for consistency of the boron and phosphorus factors, which are indeed the most common impurities. With the absence of white light, the LTFT-IR method shows only the net carrier absorption bands at an intensity proportional to the excess majority carrier concentration. These data along with the total impurities obtained with white light on the samples permitted minor adjustments to the boron or phosphorus factors, or both.

R1-2.3.2 Silicon samples whose resistivity has been carefully determined have been measured by LTFT-IR spectroscopy, and the results used to confirm or slightly modify the calibration factors.

R1-3 In 1990, a pilot study was conducted in which ten silicon samples were examined at four different laboratories by either LTFT-IR or photoluminescence, or both, and the results compared. Even though each laboratory used their own factors and modifications of this test method for determination of impurity concentrations, the data for boron and phosphorus all agreed to within ± 20% of the average value. The factors given in this test method are approximately equal to the average values from that study.

R1-4 In summary, the factors given in Table 1 are a result of continued refinement as more and better measurements have been made. However, they ultimately correspond to the resistivity measurements and the conversion to dopant (impurity) concentrations as given in SEMI MF723. The factors for boron and phosphorus have the highest degree of certainty since these two elements are the most commonly measured and are therefore studied the most. The factors for the other elements, especially aluminum, antimony, gallium, and indium, should be considered only approximations and used only to estimate their concentrations in silicon.

---

7 Irvin, J. C., "Resistivity of Bulk Silicon Diffused Layers in Silicon," *Bell System Tech. J.* **41**, 387–410 (1962).

SEMI MF1708-1104
PRACTICE FOR EVALUATION OF GRANULAR POLYSILICON BY MELTER-ZONER SPECTROSCOPIES

This guide was technically approved by the Global Silicon Wafer Committee and is the direct responsibility of the North American Silicon Wafer Committee. Current edition approved for publication by the North American Regional Standards Committee on August 16, 2004. Initially available at www.semi.org September 2004; to be published November 2004. Original edition published by ASTM International as ASTM F 1708-96. Last previous edition SEMI MF1708-02

1 Purpose

1.1 Polycrystalline silicon is used as the starting material for growth of large single crystal ingots by Czochralski methods.

1.2 Although Czochralski grown ingots are intentionally doped during crystal growth to the desired resistivity and type, the dopant levels in the polysilicon must be known to calculate the amount of dopant to be added. This practice provides a means to determine the impurity levels in granular polysilicon to be used for crystal growth.

1.3 Carbon levels in polysilicon must be known so that the concentration of carbon in the ingot can be controlled to a low level.

1.4 This practice has applicability in production control, quality assurance, materials research, and materials acceptance.

2 Scope

2.1 This practice describes a procedure to consolidate granular polysilicon into a solid rod and then to convert the polysilicon rod into a single crystal by a float-zone technique. The resultant single crystal ingot is used for the determination of trace impurities in the polysilicon. These impurities are acceptor and donor components (usually boron, aluminum, phosphorus, arsenic, and antimony) as well as substitutional carbon.

2.2 The useful range of impurity concentration covered by this practice is 0.002 to 100 parts per billion atomic (ppba) for acceptor and donor impurities, and 0.02 to 15 parts per million atomic (ppma) for carbon. The acceptor and donor impurities in a slice taken from the single crystal ingot are analyzed by photoluminescence or infrared spectroscopies. The carbon impurity is determined by analysis of a slice by infrared spectroscopy.

2.3 This practice is applicable only to evaluation of polysilicon granules as produced by thermal decomposition and deposition of silane, or one of the chlorosilanes, onto high purity seeds of polysilicon in a continuous or batch fluid bed reactor. The granules are near spherical in shape and range in size from 200 to 3000 μm with a mean size of about 900–1200 μm.

NOTICE: This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health guides and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 The quartz tubes used in this procedure must be of high purity, especially in regards to the impurities to be measured. Boron is of particular concern since it is always present in quartz and may frequently appear in uncharacteristically high concentrations in polysilicon.

3.2 All chemicals and gases used in this procedure must be free of components to be measured or they may give extraneously high results.

3.3 Loss of single crystal during the zone pass will produce an ingot that may give unsatisfactory results. The quality of the infrared or photoluminescence spectra usually reveals the lack of single crystal.

4 Referenced Standards

4.1 *SEMI Standards*

SEMI C3.42 — Specification for Argon

SEMI C28 — Specifications and Guidelines for Hydrofluoric Acid

SEMI C31 — Specification for Methanol

SEMI C34 — Specification and Guideline for Mixed Acid Etchants

SEMI C35 — Specifications and Guideline for Nitric Acid

SEMI MF1241 — Terminology of Silicon Technology

SEMI MF1389 — Test Methods for Photoluminescence Analysis of Single Crystal Silicon for III-V Impurities

SEMI MF1391 — Test Method for Substitutional Carbon Content of Silicon by Infrared Absorption

     SEMI MF1708-1104 © SEMI 2004

SEMI MF1630 — Test Method for Low Temperature FT-IR Analysis of Single Crystal Silicon for III-V Impurities

4.2 *ASTM Standard*

D 5127 — Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry [1]

4.3 *Federal Standard*

209-E — Airborne Particulate Cleanliness Classes in Cleanrooms and Clean Zones[2]

4.4 *ISO Standard*

ISO 14644–1 — Cleanrooms and associated controlled environments—Part 1: Classification of airborne particulates[3]

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 *Acronym*

5.1.1 *PTFE* — polytetrafluoroethylene, a chemically resistant polymer.

5.2 *Definitions*

5.2.1 Most terms used in this practice are defined in SEMI MF1241.

5.2.2 *Other Definitions*

5.2.2.1 *granular polysilicon*, *n* — nearly spherical, granules (200 to 3000 μm) of polysilicon as produced in a fluidized bed reactor.

5.2.2.2 *melter/zoner*, *n* — an apparatus designed to melt granular polysilicon to a solid rod and then convert the polycrystalline rod to a single crystal ingot by an rf coupled coil.

5.2.2.3 *silicon pedestal*, *n* — a piece of single crystal silicon cut from a high purity silicon ingot.

---

1 *Annual Book of ASTM Standards*, Vol 11.01, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Telephone: 610-832-9500, Fax: 610-832-9555, Website: www.astm.org

2 Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS. (This standard has been superseded by ISO 14644-1 and may no longer be available.)

3 International Organization for Standardization, ISO Central Secretariat, 1, rue de Varembé, Case postale 56, CH-1211 Geneva 20, Switzerland. Telephone: 41.22.749.01.11; Fax: 41.22.733.34.30 Website: www.iso.ch; also available in the US from American National Standards Institute, New York Office: 11 West 42nd Street, New York, NY 10036, USA. Telephone: 212.642.4900; Fax: 212.398.0023 Website: www.ansi.org, and in other countries from ISO member organizations.

6 Summary of Practice

6.1 Granular polysilicon is converted into a single crystal silicon rod in a two-step procedure.

6.1.1 First, the silicon granules are consolidated into a polysilicon rod by melting fluidized granules into the molten (bottom) end of a silicon pedestal during a downward pass of the coil of the zone furnace. After about 15 g of polysilicon has been melted and cooled in the zone process, a polysilicon rod about 8 to 12 mm in diameter and up to 70 mm in length is obtained.

6.1.2 In the second step, a single crystal silicon seed is melted into the tail end of the polycrystalline rod and a single zone pass is done in the upward direction to level the impurities and to convert the silicon to a single crystal rod. This produces a single crystal silicon ingot about 8 to 12 mm in diameter and up to 70 mm in length from which a section is sliced for measurement of impurities. The entire consolidation and zoning requires about 30 min to accomplish.

6.1.3 A slice 2 to 4 mm thick is taken from the center one-third of the single crystal silicon ingot for measurement of impurities by infrared or photoluminescence spectroscopies.

7 Apparatus

7.1 *Acid Exhaust Fume Hood —* To provide for exhaust of acid fumes, a clean air environment (ISO Class 6 minimum, as defined in ISO 14544-1), a drain for acids and water, and a deionized water supply. This hood provides for the cleaning of quartz containers, funnels, and tubes used in the melter/zoner as well as a place to etch silicon pieces and samples used in this practice.

NOTE 1: ISO class 6 is about the same as Class 1000 as defined in Federal Standard 209E).

7.2 *Laminar Flow Hood* — To provide a flow of clean (ISO Class 6 minimum) air for drying of components and the etched and clean silicon pieces.

7.3 *Quartz Sample Containers* — 200 to 300 mL capacity quartz bottles to contain and transport granular polysilicon samples.

7.4 *Quartz Funnel* — A funnel of sufficient size to transfer granular polysilicon from the sample container to the 15 mm inside diameter quartz tube.

7.5 *Quartz Tube* — A section of high purity quartz tube with 18 mm outside diameter, 15 mm inside diameter, and a length of 556 mm. The inside diameter and outside diameter variances should be small to avoid problems with clearances both internally and externally. This tube provides the working enclosure for both the consolidation and the zone leveling within the confines of the working coil of the melter/float zone apparatus.

7.6 *Melter/Float Zone Apparatus* — A radio frequency (rf) generator operating between 2.0 and 3.0 MHz with a copper, water-cooled working coil for rf coupling to the silicon (see Figure 1). The coil shall have an inside diameter of 20 mm to accommodate the 18 mm outside diameter quartz tube and shall have sufficient power to sustain a molten zone of at least 2 cm. Controls to adjust the power output of the rf generator must be readily available to the operator. The apparatus shall have a carriage to vertically support and move the quartz tube through the coil in a smooth and continuous manner. The upper and lower endpieces of the carriage shall be designed with chucks to hold silicon pedestals as well as the quartz tubing. These endpieces shall provide a seal to exclude air from the inside of the tube and have connections for argon entry at the bottom endpiece and exhaust at the top. Manual as well as motorized movement of the carriage in the vertical direction while minimizing horizontal motion is essential. This entire apparatus is set up and utilized inside a Class 6 clean room.
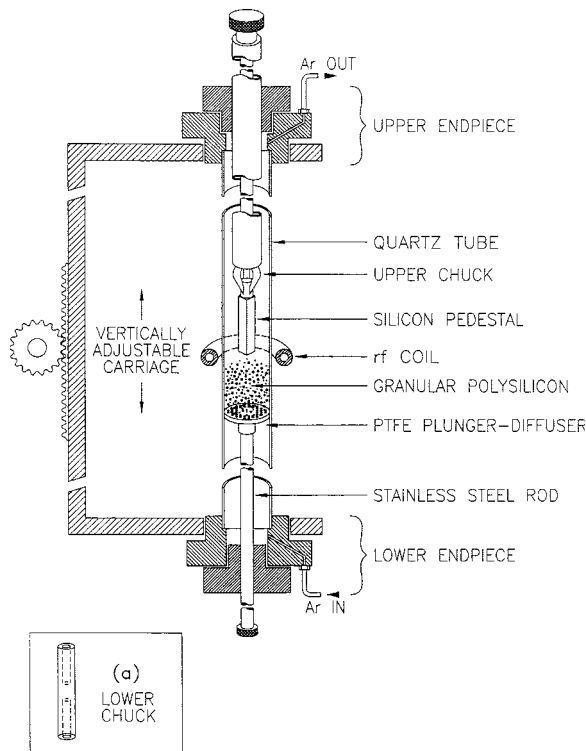

Figure 1
Melter/Float Zone Apparatus

7.7 *PTFE Plunger-Diffuser* — A cylindrical piece of PTFE machined to close tolerance that fits snugly but can be moved freely inside the quartz tube. This PTFE plunger is drilled with an array of small holes for diffusion of argon gas from the bottom endpiece of the

zoner carriage, through a bed of polysilicon granules, and finally exhausted through the top endpiece. The bottom of this plunger is machined to fit on the end of a stainless steel rod that is extended through and supported by the bottom endpiece. This rod provides a way to vertically move the PTFE plunger/diffuser plate within the quartz tube.

7.8 *Chucks* — Designed to hold silicon pedestals and seed rods.

7.8.1 *Upper Chuck* — A three-jaw chuck designed to hold a 6-mm silicon pedestal rod inside the quartz tube and supported vertically from the top carriage piece.

7.8.2 *Lower Chuck* — A cylindrical piece of stainless steel that fits inside the quartz and upon the upper end of the stainless steel rod extending from the lower endpiece with a hole drilled in the top about 3 mm inside diameter and 1 cm deep (see Figure 1). This supports a 2.5 mm single crystal silicon seed rod in a near vertical position while allowing some (about 2 mm) horizontal movement at the top of an 80 mm rod.

7.9 *Hydrogen Torch* — Constructed by restricting the end of a ¼ in. outside diameter piece of stainless steel tubing and drilling a 1.5 mm hole as the orifice. This torch is used to preheat the silicon to the point where rf coupling occurs.

7.10 *Diamond Saw* — Suitable for cutting a sample 2 to 4 mm thick from the single crystal ingot.

7.11 *Clean Room Garb* — Including gowns, gloves, lint free paper, etc.

7.12 *Polyethylene Forceps* — Size to hold 6 to 12-mm silicon slice.

7.13 *PTFE Beakers* — 100 mL in size for handling acids used in etching or cleaning.

8 Reagents and Materials

8.1 *Hydrogen Gas* — Low purity gas cylinder for hydrogen torch.

8.2 *Argon Gas* — In accordance with SEMI C3.42.

8.3 *Hydrofluoric (HF) Acid (49 %)*, in accordance with Grade 1 of SEMI C28.

8.4 *Nitric (HNO_3) Acid (70 %)* — In accordance with Grade 1 of SEMI C35.

8.5 *Mixed Acid Etchant (MAE) 57:18:25* — Composed of HF:HNO_3:Acetic Acid, in accordance with Grade 1 of SEMI C34.

8.6 *Methanol* — In accordance with Grade 1 of SEMI C31.

8.7 *Deionized (DI) Water* — Electronic grade Type E-2 as described in ASTM Guide D 5127.

8.8 *Silicon Pedestals* — 6 mm by 6 mm by 100 mm single crystalline silicon cut from high purity silicon ingots.

8.9 *Silicon Seed Rod* — 2.5 mm by 2.5 mm by 100 mm single crystal <100> silicon rod cut from high purity <100> silicon ingot.

9 Hazards

9.1 The acids used in this practice are potentially harmful and must be handled with the utmost of care at all times. Hydrofluoric acid (HF) solutions are especially hazardous to the eyes, skin, mucous membranes, and the lungs. Anyone using HF and other acids must be familiar with the potential hazards and must employ proper techniques and preventive measures to avoid injury.

9.2 The rf generator and coil of the melter-zoner apparatus can be injurious to the operator if the operator is not properly trained in working with electrical connections, rf fields, and hot parts.

9.3 Use eye protection to protect the operator from the bright light of the molten silicon in the melter-zoner apparatus.

10 Sampling

10.1 Granular polysilicon samples are best handled in clean, dry quartz bottles. Samples are always taken with clean silicon or quartz scoops or devices.

10.2 Granular polysilicon is commercially produced by a continuous process in a fluidized bed reactor. Samples for evaluation by this practice can be taken in process, while packaging (normally in 270–300 kg specially lined drums), or at the point of use. The sampling point is therefore determined by the purpose of the evaluation.

11 Reference Specimen

11.1 Use a large homogeneous sample of granular polysilicon reference material to monitor the process of consolidation and conversion to a single crystal silicon. Periodically and repeatedly convert this reference material to single crystal silicon to establish the consistency and cleanliness of this practice.

11.2 Collect and statistically evaluate the values obtained by low-temperature Fourier transform infrared spectroscopy for carbon and the acceptor and donor impurities in the analytical slices to establish and keep the process in control.

12 Preparation of Apparatus

12.1 Take the utmost care to ensure the cleanliness of all parts of the melter/zoner, especially the quartz tube, sample containers, transfer funnel, and the carriage endpieces.

12.1.1 Clean the inner part of the quartz tube and etch it with 3:1 $HF:HNO_3$. Following the acid etch, rinse the tube with copious amounts of DI water and allow it to dry in a laminar air flow hood.

12.1.1.1 **Warning:** Acids, especially HF, are very hazardous to the eyes, skin, mucous membranes, and lungs. Anyone using these acids must be familiar with and use precautionary means to avoid injury.

12.1.2 Etch, clean and dry other quartz parts, including sample containers and funnels as in Section 12.1.1 except that the etchant used is 1:1 $HF:H_2O$.

12.1.3 Carefully clean the carriage endpieces, stainless steel rods, and chucks of the melter/zoner by rinsing with methanol and allowing them to thoroughly dry in the clean room environment.

12.2 Prepare the silicon pedestals and single crystal seed rods for use by etching with a continuous stream of the MAE for 15 to 20 s, followed quickly with a copious rinse of DI water. Air dry or blot dry with lint-free paper.

13 Procedure

13.1 Assemble a freshly etched and dried quartz tube into the carriage endpieces.

NOTE 2: Freshly, as referred to here and the following paragraphs, refers to a time of less than 1 h.

13.2 Mount a freshly etched and dried silicon pedestal (6 by 6 by 100 mm) in the upper chuck and place in the upper endpiece. Center the silicon pedestal within the quartz tube. Adjust the carriage so that the bottom of the silicon pedestal is inside but not below the working rf coil. Remove the pedestal and chuck and set aside for later use.

13.3 Mount a freshly cleaned PTFE plunger-diffuser part on the lower rod assembly and place it inside the bottom of the quartz tube. Secure the rod assembly to the lower endpiece and carefully move the rod and plunger to a point of about 100 to 120 mm below the rf coil. Start the argon purge and diffuser gas flow at a rate of about 0.1 standard cubic feet per minute (SCFM) through the lower portal, PTFE diffuser, and exhaust out the top of the open quartz tube through the upper endpiece.

13.4 Introduce the granular polysilicon sample through the upper end piece with a quartz funnel. Fill with

about 25 g of polysilicon until the upper bed of granules is near the lower part of the rf coil. Reduce the argon flow until only the top layer of granules are fluidized.

13.5 Remove the funnel and replace the upper chuck and silicon pedestal. Reposition the carriage so that the pedestal is midway between the rf coil.

13.6 Ignite the hydrogen-air torch and position it slightly above and about 30 mm from the working coil impacting the outside of the quartz tube. Turn on and increase the rf power to about 80% of the operating power needed for melting. Watch for rf coupling with the silicon rod, which will occur in about 2 min as is evident from the red glow of the pedestal. Turn off the torch and move the carriage upward at a rate that the red hot zone follows the rf coil until the hot zone is at the bottom of the silicon pedestal.

13.7 Increase the rf power until the bottom of the pedestal melts. Move the position of the granules upward with the lower rod and PTFE plunger until the top of the fluidized bed begins to melt into the upper pedestal. As the granules melt into the upper pedestal, move the entire carriage upward.

NOTE 3: The melt freezes as it leaves the working zone of the rf coil. The consolidated rod diameter is smaller than the inside diameter of the quartz tube so it does not contact the tube walls.

13.8 Continue consolidation growth with minor adjustments until a consolidated polysilicon rod of about 9 mm in diameter and 60 mm in length is obtained. Lower the polysilicon granules bed and reduce the rf power permitting the tail end of the rod to solidify. Note the time required for the melting process (normally about 12 min).

13.9 Remove the lower rod and plunger from the quartz tube by removal of part of the lower endpiece. Let the excess polysilicon granules fall out the bottom of the tube and discard them.

13.10 Remove the PTFE plunger/diffuser from the lower stainless steel rod and replace it with the lower seed chuck (see Figure 1).

13.11 Mount a freshly etched and dried single crystal silicon seed (2.5 by 2.5 by 100 mm) in the lower chuck. Place the silicon seed rod, chuck, and lower rod into the quartz tube through the bottom as before. Move the lower rod upward until the seed crystal is about 5 mm below the tip of the consolidated polysilicon rod previously produced. Purge the entire tube for a minimum of 1 min at a flow rate of 0.5 SCFM.

13.12 Reduce the argon purge to about 0.1 SCFM. Reignite the hydrogen torch and increase the rf power to 80% needed to melt silicon. Watch for the glow of

the consolidated polysilicon rod as rf coupling begins. Shut off the torch.

13.13 Increase rf power until the consolidated polysilicon rod tip is molten and then raise the seed to penetrate into the melt. Hold in this position until the seed has taken sufficient heat to melt and becomes one with the melt from the consolidated polysilicon rod.

13.14 In a trial and error mode, increase the rf power as needed to carry out the one pass zone leveling. When the proper rf power is established, activate the motorized carriage for movement downward (floating zone movement is upward) at a rate to match that employed during the consolidation process, typically a zone rate of about 5.0 mm per minute. Continue the zoning until the entire consolidated polysilicon rod has been converted to a single crystal as is evident by the four growth facet lines. Now, slightly reduce the rf power and slowly move the lower rod downward separating the single crystal ingot from the polysilicon rod. Turn off the rf power. Allow about 2 min for the ingot to cool.

13.15 Remove the single crystal ingot and break off the seed crystal after scoring with a diamond scribe. Save the remaining seed for growth of the next crystal. Examine the crystal to be sure the growth facet lines extend the entire length of the ingot.

13.16 Mount the crystal in the saw chuck and cut an analytical slice 2 to 4 mm thick as needed from the center one-third of the crystal.

NOTE 4: Since segregation of the impurities occurs both during the consolidation step and the conversion to single crystal, the one pass zone during the conversion to single crystal at the same rate as the consolidation step effectively levels these impurities. Thus, the concentration of the impurities in the ingot is essentially constant except at both extremes.

13.17 Prepare the analytical slice for infrared or photoluminescence spectroscopic measurements with application of a bright chemical etch or a mechanical polish.

13.17.1 To etch, hold the slice with polyethylene forceps and suspend it into a PTFE beaker filled with the mixed acid etchant as described in Section 8.5. Gently stir the solution with a magnetic stir bar while immersing the silicon slice for 4 min. Remove and quickly rinse with copious amounts of DI water. Air dry the silicon slice, which is now ready for analysis.

13.18 Utilize the appropriate test methods for the desired analysis. For carbon content, test by infrared spectrophotometry in accordance with SEMI MF1391. For determination of donor and acceptor contents, test either by low-temperature FT-IR analysis in accordance

with SEMI MF1630 or by photoluminescence analysis in accordance with SEMI MF1389, or both.

14 Interpretation of Results

14.1 The results obtained from spectroscopic techniques on the analytical slice as obtained, directly represent the impurity concentrations in the granular polysilicon provided no impurity contamination is found during the process. In reality, there is always small impurity contamination during the consolidation and conversion to a single crystal. This contamination leads to results higher than actually present in the granular polysilicon.

15 Precision

15.1 In the mid-nineties, the precision of this practice was established by one laboratory as follows: A large sample of granular polysilicon was evaluated repeatedly and periodically by this practice for over more than a year. Low temperature Fourier transform infrared spectroscopy was used to measure the impurity concentrations. The combined errors of sample handling, consolidation to polysilicon rod, conversion to a single crystal ingot, and the infrared determinations gave a standard deviation of 0.03 ppba at the 0.06 ppba concentration level for boron and phosphorus and a standard deviation of 0.03 ppma for interstitial carbon at the 0.07 ppma level.

15.2 Analysis of more recent similar data indicates that the standard deviation is less than 0.02 ppba at the 0.04 ppba concentration level for boron and phosphorus and 0.02 ppma for interstitial carbon at the 0.05 ppma level.

16 Keywords

16.1 granular polysilicon; polycrystalline silicon; polysilicon consolidation; polysilicon evaluation; polysilicon impurities

SEMI MF1723-1104

PRACTICE FOR EVALUATION OF POLYCRYSTALLINE SILICON RODS BY FLOAT-ZONE CRYSTAL GROWTH AND SPECTROSCOPY

1 Purpose

1.1 The concentration of acceptor and donor impurities in polycrystalline silicon (polysilicon) is used by the grower of monocrystalline silicon ingots to calculate the additional dopant needed to produce the required ingot resistivity or to predict the resistivity of undoped ingots.

1.2 The concentration of acceptor and donor elements and carbon in the polysilicon is used by the crystal grower to determine material acceptance.

1.3 The concentration of impurities in the polysilicon is used for monitoring source gas purity, polysilicon production processes, development of new processes, and materials acceptance purposes.

1.4 This practice describes the sampling system and float-zone crystal growth procedures used to prepare polysilicon core samples for analysis of acceptor, donor, and carbon content.

2 Scope

2.1 This practice covers procedures for sampling polycrystalline silicon rods and growing single crystals from these samples by the float-zone technique. The resultant single crystal ingots are analyzed by spectrophotometric methods to determine the trace impurities in the polysilicon. These trace impurities are acceptor (usually boron or aluminum, or both), donor (usually phosphorus or arsenic, or both), and carbon impurities.

2.2 The useful range of impurity concentration covered by this practice is 0.002 to 100 parts per billion atomic (ppba) for acceptor and donor impurities, and 0.02 to 15 parts per million atomic (ppma) for carbon impurity. These impurities are analyzed in the ingot samples by infrared or photoluminescence spectroscopy.

2.3 This practice is applicable only to evaluation of polysilicon ingots grown by a method that utilizes a slim silicon rod (filament) upon which the polycrystalline silicon is deposited.

NOTICE: This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health guides and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 Polysilicon rods that are cracked, highly stressed, or have deep dendritic growth cannot be sampled due to shattering or breaking during the coring process.

3.2 Polysilicon cores with fractures, cracked surfaces, or voids in the surface are difficult to clean. Impurities are not completely etched out of the cracks or voids, or etch residues may remain in the cracks, thus contributing contamination. Cracked or highly stressed cores may shatter or break during the zoning process. Cores must be cleaned after fabrication to remove any oil, grease, or handling contamination.

3.3 The purity of the acids and deionized water (DI) is critically important. Impurities in the acids, etching apparatus, or water may interfere with accurate, reproducible analysis. Etching and zoning should be done in a clean room to minimize impurities from the ambient air, walls, floors, and furniture. The specific acid mixture, acid etch temperature, silicon removal rate, number of etch-rinse cycles, and exposure time are other factors that must be monitored and controlled to prevent impurity interferences. Any materials that contact the etched cores, such as boats and containers, must be cleaned before use and monitored to prevent contamination. Gloves or other materials used to wrap the etched cores must be tested and monitored to prevent contamination.

3.4 The zoner itself, especially the preheater, can introduce impurities into the growing silicon ingot. The walls, preheater, coil, and seals of the zoner are usual sources of contamination. Maintaining a clean zoner is very important to the procedures covered by this practice.

3.5 Any variation from the prescribed float-zoning procedures that can affect the distribution of the volatile impurities in the gas, liquid, and solid phases will alter the results. Variations in core diameter, zone dimensions, pull rate, seal purity, or ambient conditions may alter the effective distribution coefficient or evaporation rate and thus change the amount of impurity incorporated into the crystal.

3.6 Each acceptor or donor element and carbon have unique segregation coefficients. By growing several ingots with lengths up to 30 times the zone length, the effective segregation coefficient can be measured. These should agree with published values.[1,2] Wafers are cut from this ingot at equilibrium positions corresponding to the segregation coefficient. Wafers cut from other locations may not accurately represent the amount of impurity in the polysilicon. If ingots can not be grown to sufficient length to achieve the flat portion of the axial concentration profile, wafers can be cut from the ingot, and the measured values corrected for the effective segregation coefficient, based on repeated measurements of control rods.

3.7 In the conversion of the core to a monocrystal during zoning, it is possible to lose structure and have a zoned rod that is not monocrystalline. Ingots with excessive crystallographic defects give photoluminescence or infrared spectra with excessive noise; such spectra are difficult to interpret accurately. In extreme cases, it is not possible to obtain acceptable spectra.

4 Referenced Standards

4.1 *SEMI Standards*

SEMI C3.42 — Specification for Argon

SEMI C28 — Specifications and Guidelines for Hydrofluoric Acid

SEMI C35 — Specifications and Guideline for Nitric Acid

SEMI MF26 — Test Methods for Determining the Orientation of a Semiconductive Single Crystal

SEMI MF42 — Test Methods for Conductivity Type of Extrinsic Semiconducting Materials

SEMI MF397 — Test Method for Resistivity of Silicon Bars Using a Two-Point Probe

SEMI MF723 — Practice for Conversion Between Resistivity and Dopant Density for Boron-Doped, Phosphorus-Doped, and Arsenic-Doped Silicon

SEMI MF1241 — Terminology of Silicon Technology

SEMI MF1389 — Test Methods for Photoluminescence Analysis of Single Crystal Silicon for III-V Impurities

SEMI MF1391 — Test Method for Substitutional Carbon Content of Silicon by Infrared Absorption

SEMI MF1630 —Test Method for Low Temperature FT-IR Analysis of Single Crystal Silicon for III-V Impurities

SEMI MF1725 — Guide for Analysis of Crystallographic Perfection of Silicon Ingots

4.2 *ASTM Standard*[3]

D 5127 — Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

4.3 *Federal Standard*[4]

209-E — Airborne Particulate Cleanliness Classes in Cleanrooms and Clean Zones

4.4 *ISO Standard*[5]

ISO 14644–1 — Cleanrooms and associated controlled environments—Part 1: Classification of airborne particulates

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 *Definitions*

5.1.1 Terms related to semiconductor technology are defined in SEMI MF1241.

5.1.2 *Other Definitions*

5.1.2.1 *control rod*, n — a cylinder of polysilicon taken from a polysilicon rod with a uniform deposition layer, having known amounts of boron, phosphorus, and carbon from repeated analysis.

5.1.2.2 *core*, n — a cylinder of polysilicon obtained from a larger piece of polysilicon by drilling with a hollow diamond drill.

1 Pfann, W., *Zone Melting*, John Wiley and Sons, New York, 1958.
2 Keller, W., *et al.*, *Floating Zone Silicon*, Marcel Dekker, Inc., New York, 1981.

3 *Annual Book of ASTM Standards*, Vol 11.01, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Telephone: 610-832-9500, Fax: 610-832-9555, Website: www.astm.org

4 Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS. (This standard has been superseded by ISO 14644-1 and may no longer be available.)

5 International Organization for Standardization, ISO Central Secretariat, 1, rue de Varembé, Case postale 56, CH-1211 Geneva 20, Switzerland. Telephone: 41.22.749.01.11; Fax: 41.22.733.34.30 Website: www.iso.ch; also available in the US from American National Standards Institute, New York Office: 11 West 42nd Street, New York, NY 10036, USA. Telephone: 212.642.4900; Fax: 212.398.0023 Website: www.ansi.org, and in other countries from ISO member organizations.

5.1.2.3 *deposition layer (growth layer)*, *n* — the layer of polysilicon surrounding the filament, extending to the outer diameter of the poly rod.

5.1.2.4 *filament, slim rod*, *n* — a small diameter silicon rod, assembled into a U-shape, used to provide a substrate or seed for the deposition of polycrystalline silicon.

6 Summary of Practice

6.1 One or more core samples, selected according to a prescribed plan, are taken from the polysilicon rod to be evaluated. Cores can be taken parallel or perpendicular to the filament at both ends of the rod. The preparation and zoning process is the same for both types, but the data calculation and carbon analysis are different.

6.2 After inspection for damage, the polysilicon cores are identified and scheduled for etching and crystal growth. Cores are etched in acid, rinsed clean, mounted into a float-zone crystal growth apparatus, and converted to single crystal ingots. Cores must be float-zoned as soon as possible after being etched to avoid surface contamination. Studies in one laboratory in an ISO Class 5 (Note 1) clean room indicated that surface contamination can occur after 36 h. For each laboratory, maximum holding times and handling-packaging procedures must be determined. Cores must be reetched if the maximum holding period is exceeded. To extend the holding period, cores may be wrapped and sealed in a suitably clean material and stored in a clean environment until use.

NOTE 1: ISO Class 5 as defined in ISO 14644-1 is about the same as Class 100 as defined in Federal Standard 209E.

6.3 A control rod is etched and float-zoned along with the sample rods to monitor any contamination interferences from the sample preparation and float zoning process.

6.4 The polysilicon cores are converted to single crystal ingots by the float-zone technique, using one zone pass in an argon atmosphere. After crystal growth is completed, the ingots are checked for monocrystalline character, diameter, and length.

6.5 Sections of the ingot are selected for measurement of acceptor, donor, and carbon content, according to the individual segregation coefficients for these elements.

6.6 From the selected sections of the ingot, wafers are cut and prepared for analysis by spectrophotometric techniques described in SEMI MF1389, SEMI MF1391, and SEMI MF1630.

7 Apparatus

7.1 *Coring Equipment*

7.1.1 *Drill Press* — With water cooling capability.

7.1.2 *Diamond Core Drill* — Bit sized to produce a 20 mm diameter (approximate) polysilicon core at least 100 mm in length for parallel cores and a length suitable to drill completely through the rod diameter for perpendicular cores. Drill diameters of 3 mm or 5 mm are used for seed preparation.

7.2 *Etching Equipment*

7.2.1 *Etch Bench* — Located in an ISO Class 6 Clean Room, as defined in ISO 14644-1, to minimize ambient contamination, with adequate exhaust for acid fumes, tanks for etching acid and DI water rinsing, and facility for drying samples in a clean environment.

NOTE 2: ISO Class 6 is about the same as Class 1000 as defined in Federal Standard 209E.

7.2.2 *Quartz Boats* — Or other acid-resistant material, such as polytetrafluoroethylene, designed to hold poly-silicon rods of the specified diameter and length, during the etching, rinsing, and drying process.

7.3 *Float Zone Crystal Growth Equipment*

7.3.1 *Float Zone Crystal Growth Furnace* — With an inert gas atmosphere, and water-cooled chamber of sufficient size to accommodate growth of ingots of specified diameter and length, located in a clean room of ISO Class 6 or better. The apparatus shall allow relative vertical motion of the work, with respect to the coil, with no significant lateral motion. This vertical motion may be accomplished by screw, cable, or hydraulic mechanisms. In addition, there shall be a shaft to support the core sample and a shaft to support the seed. At least one shaft shall be capable of vertical displacement relative to the other. The seed shaft shall be rotated about its longitudinal axis as a precaution against thermal and solute asymmetries in the molten zone. Either the sample or seed chuck shall be free to slip with respect to the rotation in the event of freezing of the molten zone. The sample and seed chucks shall be of molybdenum, tantalum, tungsten, or quartz to minimize contamination of the silicon. The coil design and power control shall maintain a stable, completely molten zone during the entire growth process. Materials used in the apparatus shall have vapor pressures less than 1×10^{-6} torr under operating conditions. The susceptor (preheater) shall be about the same diameter as the sample core and made of tantalum, or other material that minimize the contamination of the silicon.

7.3.2 *Scale* — Calibrated in mm, suitable for accurate measurement of ingot length and marking locations in the ingot for cutting.

7.3.3 *Wire Brush* — Made of stainless steel, suitable for cleaning the inside of the chamber of the vacuum zoner, with a handle long enough to reach the length of the chamber.

7.3.4 *Vacuum Cleaner* — Suitable for clean room use, with flexible hose and narrow nozzle.

7.3.5 *Clean Room Gloves* — Gowns, Masks, Hoods, Wipes, and other clean room materials.

7.3.6 *Wafering Saw* — Suitable for cutting wafer samples, about 2-mm thick, from the ingot.

8 Reagents

8.1 *Nitric Acid* (HNO_3) — In accordance with Grade 2 of SEMI C35.

8.2 *Hydrofluoric Acid* (HF) — In accordance with Grade 2 of SEMI C28.

8.3 *Acid Etching Mixture* — Typically 4 to 1 to 8 to 1 HNO_3 to HF.

8.4 *Deionized Water* — With a purity equal to or greater than that specified for Type E-2 in ASTM D 5127.

8.5 *Argon Purge Gas* — In accordance with SEMI C3.42.

9 Hazards

9.1 It is required that the user have a working knowledge of fabrication techniques, acid handling practices, and crystal growth furnaces. Good laboratory practices also must be understood.

9.2 This practice uses hot acid to etch away the surface of the polysilicon rod. The etchant is potentially harmful and must be handled in an acid exhaust fume hood with utmost care at all times. Hydrofluoric acid solutions are particularly hazardous. All precautions normally used with these acids should be strictly observed. They should not be used by anyone who is not familiar with the specific preventative measures and first aid treatments given in the appropriate Material Safety Data Sheet.

9.3 The crystal growth furnace uses radio frequency (RF) power (generator and coil) to supply power for melting silicon, about 1400°C. The user must be trained in working with electrical connections, pressurized gas lines, RF fields, and hot parts.

9.4 The molten silicon in the melt zone emits a bright light and operators may be exposed to this light for several hours. This exposure requires the use of eye protection.

10 Sampling

10.1 The cores shall contain material representative of the growth process used to form the polysilicon rod. The cores are intended to be representative of the polysilicon rod being sampled.

10.2 A number of cores can be taken at different locations of the polysilicon rod to satisfy various sample plans. Samples taken should cover both ends of the rod. Two typical sampling methods are taking cores parallel to the filament and taking cores perpendicular to the filament as shown in Figures 1 and 2. The parallel core system is described in Section 10.2.1. The perpendicular core system is described in Section 10.2.2.
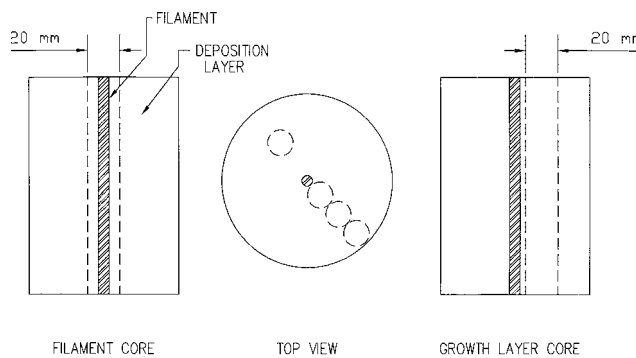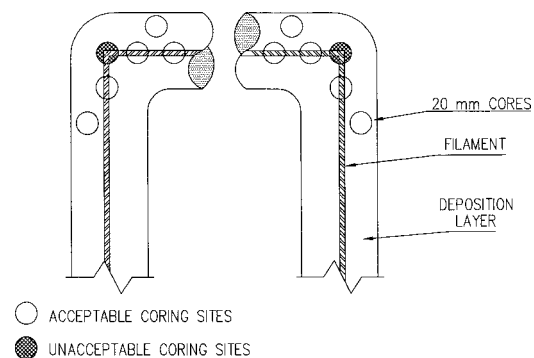

Figure 1
Parallel Coring Location

Figure 2
Perpendicular Coring Locations

10.2.1 *Parallel Cores* — As shown in Figure 1, cores are taken parallel to the filament at a minimum length of 100 mm and a diameter of 20 mm. Two different cores, a filament core and a growth layer core, are required to calculate the total polysilicon rod impurity content.

10.2.1.1 *Parallel Filament Cores* — Cores including the filament are representative of the filament and the initial deposition layer on the filament. These cores are float zoned, analyzed, and the values combined with the growth layer cores to calculate a total value.

10.2.1.2 *Parallel Growth Layer Cores* — Cores not including the filament, only the growth layer, are representative of the poly deposited onto the filament. These cores are float-zoned, analyzed, and the values combined with the filament core values to calculate a total value.

10.2.1.3 *Parallel Core Sampling Locations*

10.2.1.3.1 *Radial Location* — Cores can be taken across the entire rod diameter to check radial uniformity of the deposition layer. Since the outer surface may contain surface cracks or surface roughness, the outer 5 mm should not be sampled.

10.2.1.3.2 *Axial Location* — For an entire U-rod of polysilicon, cores usually are taken from the short bridging section or from a region on the long rod within 50 mm of either end, but may be taken at any location to check axial uniformity of deposition.

10.2.2 *Perpendicular Cores* — As shown in Figure 2, 20-mm diameter cores are taken through the diameter of the polysilicon rod with length same as the diameter of the poly rod. Cores are taken so that the filament and material from all parts of the deposition layer are included. For accurate calculation of the impurities at various growth layers, at least one end of the perpendicular core should include the outer skin layer. For rods less than 60-mm diameter, it is not possible to produce single crystal ingots of sufficient zone length for accurate analysis. In this case, cores parallel to the filament are taken for analysis.

10.2.2.1 *Perpendicular Growth Layer Cores* — Cores without the intersected filament, as shown in Figure 2, can be zoned and analyzed to determine the impurities in the deposition layer. To find the impurities in the total rod, the filament must be analyzed separately and combined with the growth layer results. Values are calculated using the formulas for parallel cores.

10.2.2.2 *Perpendicular Core Sampling Location* — For an entire U-rod of polysilicon, cores usually are taken from the short bridging section, or from a region on the long rod within 50 mm of either end. Cores may be taken at any location to check axial uniformity of deposition, but are not taken at the bend of the U-rod, due to stresses in this area.

10.3 *Filament Analysis* — If a parallel or perpendicular filament core can not be taken, the filament may be analyzed separately, then combined with the growth layer analysis. For filaments that are single crystal, or nearly single crystal, wafers can be cut, prepared, and analyzed by spectrophotometric techniques described in SEMI MF1389, SEMI MF1391, and SEMI MF1630.

11 Reference Specimens

11.1 Use polysilicon control rods to monitor the purity of the core preparation techniques, acid etch bath, and zoning conditions. Drill a large number of deposition layer cores, 20-mm diameter by 100-mm length from polysilicon rods having a uniform deposition layer. Select control rods with low impurity levels, such as acceptor/donor values about 0.01 ppba and carbon values about 0.05 ppma to allow the early detection of trace impurities from interference sources. After repeated analysis, assign values for donor, acceptor, and carbon concentrations. Then etch, zone, and analyze these control rods on a periodic basis to monitor purity of the sample preparation, etching, and zoning processes.

11.2 Control chart values for the acceptor, donor, and carbon concentrations from the control rods using standard statistical process-control techniques and statistical rules to determine if the current values are in control. If these values exceed the statistical limits, make corrections and repeat the analysis.

12 Procedure

12.1 *Seed Preparation*

12.1.1 Prepare round or rectangular seeds by core drilling, cutting, or crystal pulling from high purity float zone ingots. Use seed material of zero dislocation density with acceptor content less than 0.05 ppba, donor content less than 0.05 ppba, and carbon content less than 0.1 ppma.

12.1.2 Select a high purity single crystal seed, 3 mm to 5 mm in diameter, for initiation of float zone crystal growth. Orient the seed $\langle 111 \rangle$ within 0.5°.

12.1.3 Clean, acid etch, rinse and dry the seed to the same procedure, using the same equipment described for core samples. To avoid surface contamination, use seeds within 36 h after etching, or store them in a manner to prevent contamination.

12.2 Core Etching

12.2.1 Do all operations in the etch bench clean room and zoner clean room with operators in full clean room attire, including gloves, hood, and mask.

12.2.2 Make a fresh acid etch mixture and fill the tanks in the etch bench. When the proper temperatures and water flows are achieved, place the core samples into clean etch boats and etch, rinse, and dry the cores. Use the HNO_3-HF acid etching mixture, etching at least two cycles, to remove a minimum of 100 μm from the surface of the core sample. This is necessary in order to remove surface damage caused by the coring process. Other acid etch mixtures can be used, but must be evaluated and controlled to ensure effectiveness and avoid impurity interferences.

12.2.3 After etching, float zone cores as soon as possible to reduce the probability of contamination. Re-etch cores if the maximum holding period is exceeded. To extend the holding period, seal the cores in a suitably clean material and store in a clean room environment.

12.3 Preparation of Apparatus

12.3.1 Clean the core drilling apparatus to prevent contamination of the core sample.

12.3.2 Clean the etch bench and check the DI rinse water purity, temperature, total organic carbon, and resistivity.

12.3.3 Clean the float zone chamber. Using the stainless steel wire brush, scrub the walls of the chamber to loosen silicon deposits and remove the loose particles with the vacuum cleaner. Wipe the walls, holders, and coil with clean room wipes soaked with a high purity solvent. Inspect cooling water reservoir, water flow, water temperature, coil and preheater connections, shaft, coil feedthroughs, door seals, hose connections, travel stops, and rotations.

12.3.4 Carry out major cleaning, including acid cleaning of coil and associated parts, and changing of seals on a periodic basis. After cleaning, argon drying, and vacuum pumping, perform a chamber and preheater bakeout of at least 15 min.

12.4 Ingot Growth

12.4.1 Place the core samples and seed in the furnace chamber so that both hang plumb and are centered and aligned with the vertical axis of rotation.

12.4.2 Remove air from the chamber with a series of evacuation and argon purge cycles. Fill the chamber with argon and continue the argon purge throughout the growth cycle, maintaining a positive pressure of argon in the chamber.

12.4.3 Position the seed end of the core sample in the coil, and the preheater close to the seed end of the core. Adjust the preheater power to make the initial induction coupling of the preheater and sample, and heat until the sample begins to glow, about 600 to 700°C. Move the preheater away from the sample and move the core sample close to the coil opening to establish a molten zone controlled by power to the coil.

12.4.4 After a small molten zone has been established at the seed end, move the seed vertically until it touches the molten zone. Withdraw the seed to form a conical melt, making sure the seed has melted in, and begin the necking phase in order to form a zero dislocation crystal.

12.4.5 Adjust top and bottom travel and rotation rates to complete the necking phase, check for the three-growth facet lines to ensure the ingot is single crystal, and adjust travel and power level to form the final diameter of the ingot. Adjust the travel and rotations and grow a single crystal zero dislocation ingot.

12.4.6 When the desired ingot length has been attained, pull the ingot from the melt, making sure the ingot and melt separate without freezing. After separation, reduce power, stop all travels and rotation, turn off power, and allow to cool.

12.5 Ingot Evaluation

12.5.1 *Visual Examination* — Examine the ingot visually for uniformity of diameter, continuous uniform-growth facet line, and color, to determine whether the ingot is zero dislocation single crystal and whether oxide deposits are present as a result of air leaks.

12.5.2 *Structural and Electrical Examination*

12.5.2.1 Determine crystallographic orientation in accordance with SEMI MF26 on a sampling basis to confirm the visual examination.

12.5.2.2 Determine the crystallographic perfection of the grown ingot in accordance with SEMI MF1725 on a sampling basis to confirm the visual examination.

12.5.2.3 Test for uniform distribution of acceptor/donor impurities by plotting a resistivity profile along the length of the ingot in accordance with SEMI MF397. Note that resistivity values should vary along the length consistent with the net acceptor/donor values measured at the various points and that sharp changes in the profile indicate point contamination or nonuniformity of the sample deposition layer.

12.6 Ingot Sampling

12.6.1 After the ingot is inspected for crystallographic perfection, appearance, and uniformity, and judged to