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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Practice for Evaluation of Polycrystalline Silicon Rods by Float-Zone Crystal Growth and Spectroscopy[1]

This standard is issued under the fixed designation F 1723; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

This practice replaces Method F 574, and Practice F 41. Method F 574 and Practice F 41 are obsolete, describing multi-pass zoning and vacuum zoning practices, and resistivity measurements for the calculation of impurity concentrations. One pass zoning and analysis by spectrophotometric techniques to identify and quantify the acceptor and donor elements have replaced the obsolete methods. Expanded sampling plans, the use of reference specimens, and practices for sampling of ingots are improvements made to these standards.

1. Scope

1.1 This practice recommends 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 polysilicon. These trace impurities are acceptor (usually boron or aluminum, or both), donor (usually phosphorus or arsenic, or both), and carbon impurities.

1.2 The useful range of impurity concentration covered by this practice is 0.002 to 100 parts/billion atomic (ppba) for acceptor and donor impurities, and 0.05 to 5 parts/million atomic (ppma) for carbon impurity. These impurities are analyzed in the ingot samples by infrared or photoluminescence spectroscopy.

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

1.4 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 particularly are hazardous and 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.

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

2. Referenced Documents

2.1 *ASTM Standards:*

D 5127 Guide for Electronic Grade Water[2]

F 26 Test Methods for Determining the Orientation of a Semiconductive Single Crystal[3]

F 47 Test Method for Crystallographic Perfection of Silicon by Preferential Etch Techniques[3]

F 397 Test Method for Resistivity of Silicon Bars Using a Two-Point Probe[3]

F 723 Practice for Conversion Between Resistivity and Dopant Density for Boron-Doped and Phosphorus-Doped Silicon[3]

F 1241 Terminology of Silicon Technology[3]

F 1389 Test Method for Photoluminescence Analysis of Single Crystal Silicon for III-V Impurities[3]

F 1391 Test Method for Substitutional Carbon Content of Silicon by Infrared Absorption[3]

F 1630 Test Method for Low Temperature FT-IR Analysis of Single Crystal Silicon for III-V Impurities[3]

2.2 *Federal Standards:*

Federal Standard 209E Airborne Particulate Cleanliness Classes in Cleanrooms and Clean Zones[4]

2.3 *SEMI Standards:*

C 3 Specification for Gases[5]

C 7 Specification for Reagents[5]

3. Terminology

3.1 *Definitions:* Terms used in this practice are defined in Terminology F 1241 or below.

[1] This practice is under the jurisdiction of ASTM Committee F-1 on Electronicsand is the direct responsibility of Subcommittee F01.06 on Silicon Materials and Process Control.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 10.05.

[4] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

[5] Book of SEMI Standards, available from Semiconductor Equipment and Materials International, 805 E. Middlefield Road, Mountain View, CA 94043.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *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.

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

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

3.2.4 *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.

4. Summary of Practices

4.1 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. The preparation and zoning process is the same for both types, but the data calculation and carbon analysis are different.

4.2 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 a Class 100 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.

4.3 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.

4.4 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.

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

4.6 From the selected sections of the ingot, wafers are cut and prepared for analysis by spectrophotometric techniques described in Test Methods F 1389, F 1391, and F 1630.

5. Significance and Use

5.1 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.

5.2 The concentration of acceptor and donor impurities in the polysilicon is used by the crystal grower to calculate the additional dopant needed to produce the required ingot resistivity or predict the resistivity of undoped ingots.

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

5.4 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.

6. Interferences

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

6.2 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.

6.3 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.

6.4 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.

6.5 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.

6.6 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.[6,7] 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 poly. 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

[6] Pfann, W., *Zone Melting*, John Wiley and Sons, New York, 1958.

[7] Keller, W., et al., *Floating Zone Silicon*, Marcel Dekker, Inc., New York, 1981.

on repeated measurements of control rods.

6.7 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.

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 a Class 1000 Clean Room, as defined in Federal Standard 209E, 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.

7.2.2 *Quartz Boats*, or other acid-resistant material, such as polytetrafluoroethylene, designed to hold polysilicon 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 Class 1000 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 either 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 will 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 *Electronic Grade Acids*, in accordance with SEMI Specification C 7.

8.1.1 *Nitric Acid* (HNO_3).

8.1.2 *Hydrofluoric Acid* (HF).

8.1.3 *Acid Etching Mixture*, typically 4 to 1 to 8 to 1 HNO_3 to HF.

8.2 *Deionized Water*, with a resistivity equal to or greater than that specified for Guide D 5127, Type E-2.

8.3 *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 The acids used in this evaluation procedure are potentially harmful and must be handled in a fume hood with the 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 preventive 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. Two typical sampling methods are taking cores parallel to the filament and taking cores perpendicular to the filament as shown in Fig. 1 and Fig. 2. The parallel core system is described in 10.2.1. The perpendicular core system is described in 10.2.2.

10.2.1 *Parallel Cores*— As shown in Fig. 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

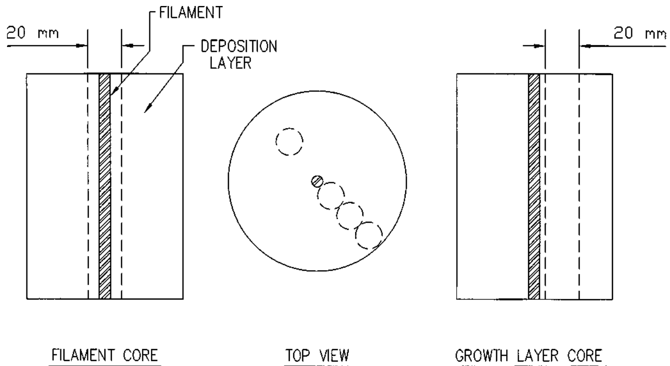

FIG. 1 Parallel Core Coring Locations

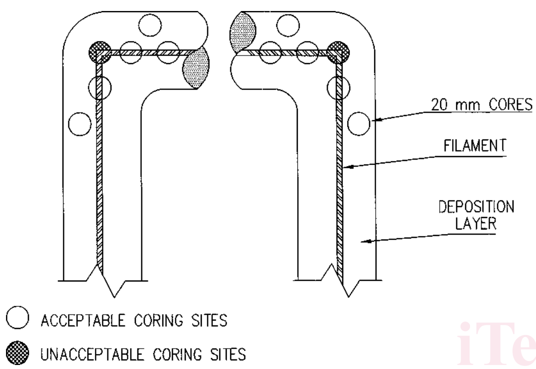

FIG. 2 Perpendicular Core Coring Locations

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.

10.2.2 *Parallel Core Sampling Locations*:

10.2.2.1 *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.

10.2.2.2 *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.

10.2.3 *Perpendicular Cores*—As shown in Fig. 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.

10.2.3.1 *Perpendicular Growth Layer Cores*—Cores without the intersected filament, as shown in Fig. 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.

10.2.3.2 *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 Test Methods F 1389, F 1391, and F 1630.

11. Reference Specimens

11.1 In order to monitor the purity of the core preparation techniques, acid etch bath, and zoning conditions, polysilicon control rods are used. A large number of deposition layer cores, 20-mm diameter by 100-mm length, are drilled from polysilicon rods having a uniform deposition layer. After repeated analysis, values can be assigned for donor, acceptor, and carbon. Selecting control rods with low impurity levels, such as acceptor/donor values about 0.01 ppba and carbon values about 0.05 ppma allows the early detection of trace impurities from interference sources. These control rods then are etched, zoned, and analyzed on a periodic basis to monitor purity of the sample preparation, etching, and zoning processes.

11.2 Values for acceptor, donor, and carbon from the control rods are control charted using standard statistical process-control techniques, and statistical rules established to determine if the current values are in control. If these values exceed the statistical limits, corrections must be made and the analysis must be repeated.

12. Procedure

12.1 *Seed Preparation*:

12.1.1 Select a high purity single crystal seed, 3-mm to 5-mm diameter, for initiation of float zone crystal growth. Orient the seed ⟨ 111⟩ within 0.5°. Seeds are prepared by core drilling, cutting, or crystal pulling from high purity float zone ingots and can be round or rectangular at different sizes. 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 Clean, acid etch, rinse and dry the seed to the same procedure, using the same equipment described for core samples. To avoid surface contamination, seeds must be used within 36 h after etching, or stored 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