



Standard Practice for Evaluation of Polycrystalline Silicon Rods by Float-Zone Crystal Growth and Spectroscopy¹

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 Water²
- F 26 Test Methods for Determining the Orientation of a Semiconductive Single Crystal³
- F 47 Test Method for Crystallographic Perfection of Silicon by Preferential Etch Techniques³
- F 397 Test Method for Resistivity of Silicon Bars Using a Two-Point Probe³
- F 723 Practice for Conversion Between Resistivity and Dopant Density for Boron-Doped and Phosphorus-Doped Silicon³
- F 1241 Terminology of Silicon Technology³
- F 1389 Test Method for Photoluminescence Analysis of Single Crystal Silicon for III-V Impurities³
- F 1391 Test Method for Substitutional Carbon Content of Silicon by Infrared Absorption³
- F 1630 Test Method for Low Temperature FT-IR Analysis of Single Crystal Silicon for III-V Impurities³

2.2 Federal Standards:

- Federal Standard 209E Airborne Particulate Cleanliness Classes in Cleanrooms and Clean Zones⁴

2.3 SEMI Standards:

- C 3 Specification for Gases⁵
- C 7 Specification for Reagents⁵

3. Terminology

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

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.

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

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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

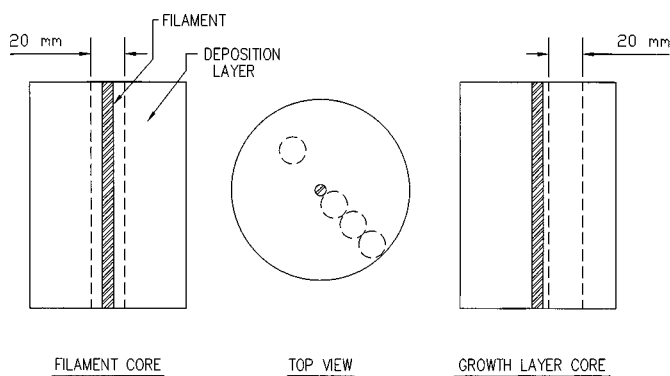


FIG. 1 Parallel Core Coring Locations

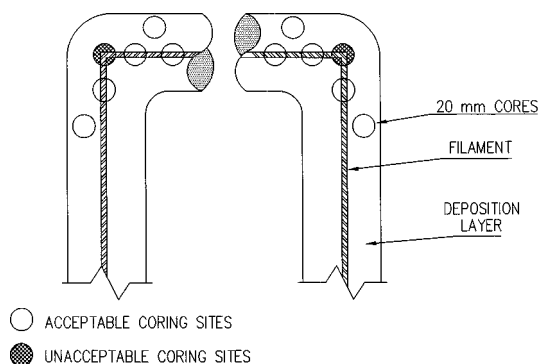


FIG. 2 Perpendicular Core Coring Locations

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 $\langle 111 \rangle$ 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

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. After etching, cores must be float zoned as soon as possible to reduce the probability of contamination. Cores must be reetched 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. Major cleaning, including acid cleaning of coil and associated parts, and changing of seals is done 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. By interpreting the appearance of the liquid/solid interface, the melt diameter and the melt characteristics, and adjusting the travel and rotations, a single crystal zero dislocation ingot can be grown.

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 by Test Method F 26. This can be done on a sampling basis to confirm the visual examination.

12.5.2.2 Determine the crystallographic perfection of the grown ingot by Test Method F 47. This can be done 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 according to Test Method F 397. Resistivity values should vary along the length consistent with the net acceptor/donor values measured at the various points. 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 be acceptable, choose sampling points for acceptor, donor, and carbon sample wafers. Cut the sample wafers at the proper points, then analyze for acceptor and donor content by Test Methods F 1389 and F 1630, and for carbon by Test Method F 1391. Preparation of the samples for these methods is described in each method. Wafers about 2-mm thick are cut from the ingot for these analyses. Ingot sampling plans are different for the parallel and the perpendicular cores, as discussed in 12.6.2 and 12.6.3.

12.6.2 *Parallel Cores*—For parallel cores (10.2.1), single crystal ingot size is about 10-mm diameter by about 200-mm length. Select the sampling points according to the individual segregation coefficients for the specific impurities so these are representative of more than 90 % of the impurity concentration as follows:

12.6.2.1 *Segregation Effects*—During the growth of the crystal, crystallization from the melt, the impurity concentration in the solid phase is different from that of the liquid phase due to segregation.^{6,7} The different impurities have different segregation coefficients, defined as:

$$K_o = \frac{C_s}{C_l}$$

where:

K_o = equilibrium segregation coefficient,

C_s = concentration of the impurity in the solid phase, in atoms/cm³, and

C_l = concentration of the impurity in the liquid phase, in atoms/cm³.

12.6.2.2 The equilibrium segregation coefficient is not used for calculations since it is applicable only for solidification at a negligibly slow growth rate. For higher solidification rates, the impurity atoms are rejected by the advancing melt at a greater rate than they can diffuse into the melt. The impurity atoms accumulate in the melt layer near the growth interface, developing an impurity concentration gradient. The concentration of this gradient depends on the growth rate, fluid

flow in the melt, and diffusion behavior of the dopant. An effective segregation coefficient, K_{eff} , is described as:

$$K_{eff} = \frac{K_o}{K_o + (1 - K_o)\exp(-V\delta/D)}$$

where:

- V = the growth rate, in cm/s,
- δ = the diffusion layer thickness, in cm, and
- D = the diffusion coefficient of the impurity in the melt, in cm^2/s .

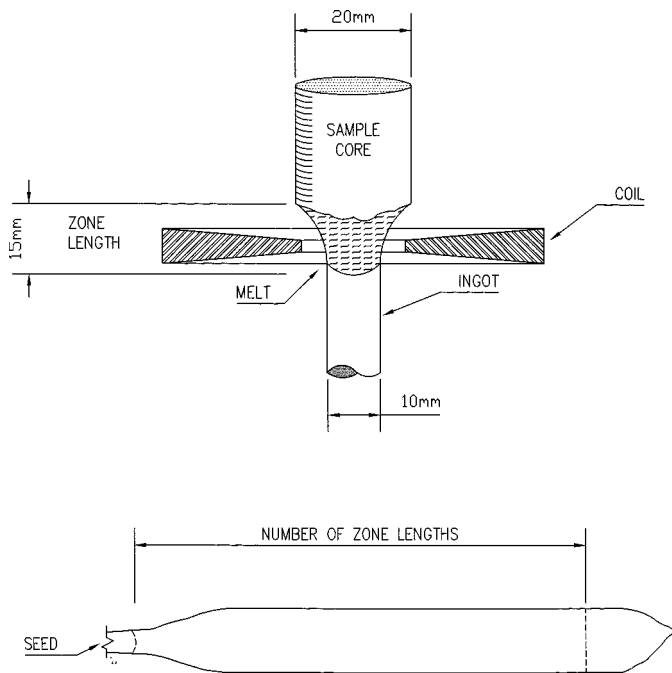
12.6.2.3 In practice, a doping profile is measured to determine the concentrations of impurities along the length of the ingot. The zone length, shown in Fig. 3, is dependent on sample diameter, coil design, and pull rate. After initial determination of the zone length, this is remeasured only after changes occur in the method and apparatus. The doping profile, measured for each impurity, determines where the ingot should be cut to provide accurate impurity values. Sample points should be chosen to be representative of more than 90 % of the impurity concentration. In Fig. 3, the zone length is measured at 15 mm. If the doping profile indicates that the flat portion of the curve is at 12-zone lengths for an impurity, the sample is taken at 12-zone lengths (12 by 15 mm = 180 mm) from the start of solidification on the ingot.

12.6.2.4 *Ingot Profiling*—For the type of float zone furnace, coil design, pull rates, and ingot/core sample diameter used, the effective segregation coefficient for the impurities can vary. To calibrate the individual zoner parameters and technique used, the actual segregation coefficient profile is measured. For example, to determine the carbon profile, an ingot is cut into wafers along its length, and carbon measured in each of the wafers. A plot is made then of carbon concentration versus zone length. The number of zone lengths required to reach the flat portion of the axial concentration profile determines the

length of ingot that must be grown to achieve an accurate carbon value. Fig. 4 shows an axial doping profile for carbon where a 20-mm diameter sample core was zoned to a 10-mm diameter ingot with a zone length of 15 mm. The effective segregation coefficient was 0.175. In this case, growing the ingot to a zone length of 12 ensures that the maximum amount of carbon has been incorporated into the ingot. Sampling the ingot for carbon at a zone length of 12 gives reproducible carbon values that accurately reflect the amount of carbon in the polysilicon sample.

12.6.2.5 *Slice Locations*—Once the concentration gradient for each element for the individual zoner conditions is established, sampling rules are established for each element. Boron, with a high segregation coefficient, will have a relatively flat profile. A wafer taken from the ingot at 6-zone lengths has a value nearly equal to that taken at 12-zone lengths. If one value is significantly higher than the other, a contamination has probably occurred, and the analysis should be repeated. Phosphorus, with a smaller segregation coefficient, will have different values at the 6 and 12-zone length points. The midpoint should have a value about 10 to 15 % lower than the end point. If not, contamination is indicated and the analysis should be repeated. Carbon, with a low segregation coefficient, will vary greatly between the 6 and 12-zone length points. If not, contamination is indicated and the analysis should be repeated. Carbon value at the maximum ingot length should be reported.

12.6.3 *Perpendicular Cores*—For perpendicular cores (10.2.2), single crystal ingot size is about 14-mm diameter with a length determined by the poly rod diameter, about 100 mm. For these ingots, sampling for acceptor-donor content is different than the carbon sampling, due to the small segregation



FOR 12 ZONE LENGTHS (12 x 15mm = 180mm), CUT INGOT AT 180 mm.

FIG. 3 Zone Length Measurement and Ingot Sampling Point

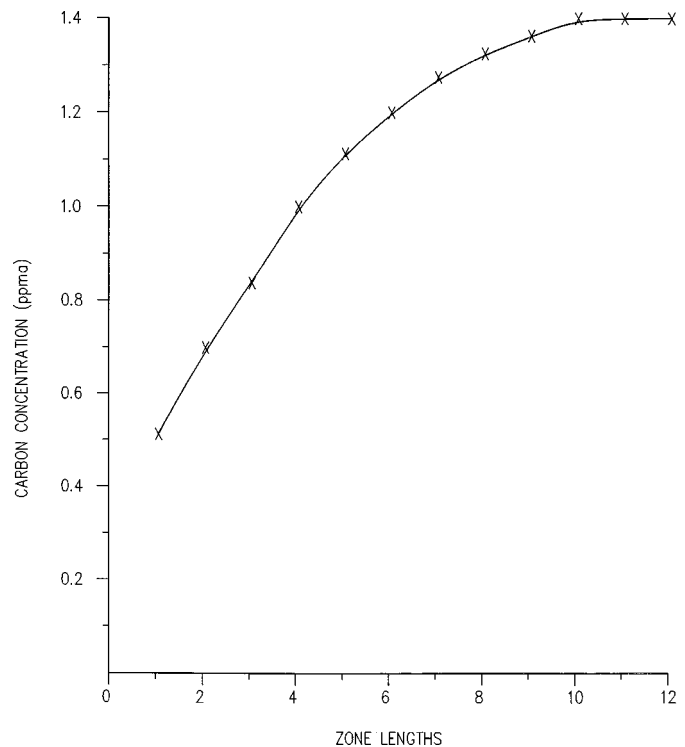


FIG. 4 Axial Doping Profile for Carbon

coefficient for carbon. Sampling points are selected according to the following:

12.6.3.1 *Resistivity Profile*—Determine the distribution of acceptor/donor impurities along the length of the ingot by plotting a resistivity profile of the ingot at 10-mm intervals, in accordance with Test Method F 397. Conductivity type, in accordance with Test Method F 42, is also profiled for the ingot, at 10-mm intervals. Due to the segregation effects discussed in 12.6.2.1, characteristic purity of the filament, and other interferences discussed in Section 6, the resistivity profile will differ between laboratories. A typical resistivity/type profile is established after repeated runs on control rods and production samples. Significant variation in the resistivity profile indicates point contamination or nonuniformity of the deposition layer.

12.6.3.2 *Slice Locations*— Sampling rules for each element are established based on the resistivity/type profile. The single crystal ingot length is correlated to the polysilicon rod diameter, and a slice taken at the representative midpoint between the filament and the outer skin of the polysilicon rod. This wafer is analyzed for acceptor/donor values in accordance with Test Method F 1389 or Test Method F 1630. For the cross section of a polysilicon rod, these values represent the R/2 location. If the resistivity/type profile has significant variation from the standard profile, other locations may be sampled to determine the distribution of each impurity. For ingots with significant variation suggesting point contamination, the analysis must be repeated.

12.6.3.3 *Carbon Analysis*— Since accurate carbon values can not be obtained on short ingot lengths, the analysis is done on polysilicon sections that have been annealed.⁸ A second perpendicular polysilicon core sample is taken and annealed at approximately 1360°C for 2 h. Two 2-mm thick slices are taken for the carbon measurement in accordance with Test Method F 1391. One sample is taken from the point representative of the midpoint of the growth layer, the other sample taken at the point representative of the filament location. Other locations may be sampled for measurement of radial distribution.

13. Calculations

13.1 After measurement of the acceptor, donor, and carbon impurities in the cut wafers, relate these values to the levels in the polysilicon by making the following calculations.

13.2 *Parallel Cores*— For the sampling procedure of Fig. 1, 10.2.1, parallel cores, in cases where the filament may be doped, or have a different composition than the deposition layer, make the following calculation in order to determine values for the total rod product.

$$\text{Concentration (Total Rod Product)} = \frac{(A_f \times C_f) + (A_t - A_f)(C_{D.L.})}{A_t}$$

where:

A_f = area of filament, in cm^2 ,
 C_f = concentration of impurity in the filament, in ppba for donor and acceptor, in ppma for carbon,
 A_t = area of polysilicon rod, in cm^2 , and
 $C_{D.L.}$ = concentration of impurity in deposition layer, in ppba for donor and acceptor, in ppma for carbon.

13.2.1 This calculation assumes that the deposition layer is uniform across the diameter of the polysilicon rod. This can be demonstrated by taking sufficient core samples to cover the entire deposition layer.

13.3 *Perpendicular Cores*—For the sampling procedure of Fig. 2, 10.2.2, perpendicular cores, where ingots have been grown as in 12.6.3, make the following calculation in order to determine values for the total rod product.

13.3.1 Correlate the single crystal ingot length to the polysilicon rod cross section as shown in Fig. 5. A zone length is related to a cross section area. Boron, with a large segregation coefficient, is assumed to have an even distribution throughout the entire cross section. Phosphorus, with a smaller segregation coefficient, needs to be corrected for segregation factor for each zone length across the cross section. Effective segregation coefficient for phosphorus, based on repeated measurements of control rods for a specific sample diameter, coil design, and pull rate, needs to be determined by each laboratory. At one laboratory, segregation factors, based on an effective segregation factor of 0.5, were calculated for the zone lengths of Fig. 5 as follows:

Zone Length	Segregation Factor
1	0.697
2	0.816
3	0.888
4	0.932
5	0.959
6	0.975
7	0.985
8	0.991

13.3.2 Spectrophotometric values for boron (see Test Method F 1389 or F 1630) are used directly in the following formula to calculate the total boron concentration in the total rod product. Values for arsenic and aluminum also are obtained from photoluminescence or FT-IR measurement and, if greater than detection limit, must be corrected by a measured segregation coefficient. Bulk phosphorus value is obtained by photoluminescence measurement at the midpoint between the filament and the outer skin. Volume averaged phosphorus is calculated from the resistivity profile measurement of 12.6.3.1. All values must be corrected for the segregation factor before using in the following formula. For calculation of volume averaged phosphorus values from the resistivity data, according to Practice F 723 in the 100 to 5000 ohm cm resistivity range, the conversion factor for phosphorus is approximately 85.

⁸ Hwang, L. L., Bucci, J., McCormick, J. R., "Measurement of Carbon Concentration in Polysilicon Using FTIR," *Journal of the Electrochemical Society*, Vol 138, No. 2, 1991, pp. 576.

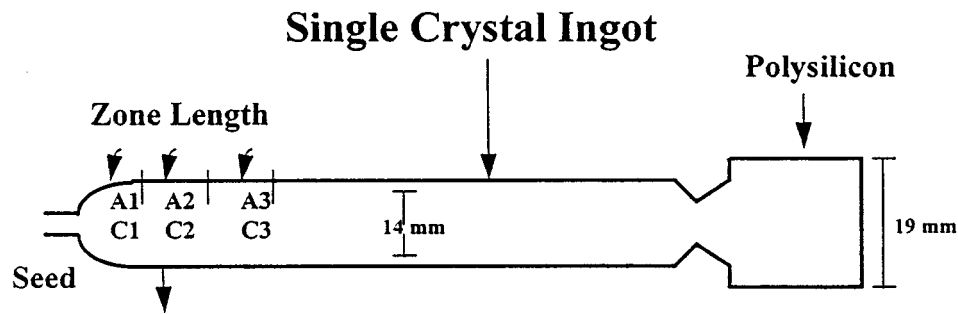
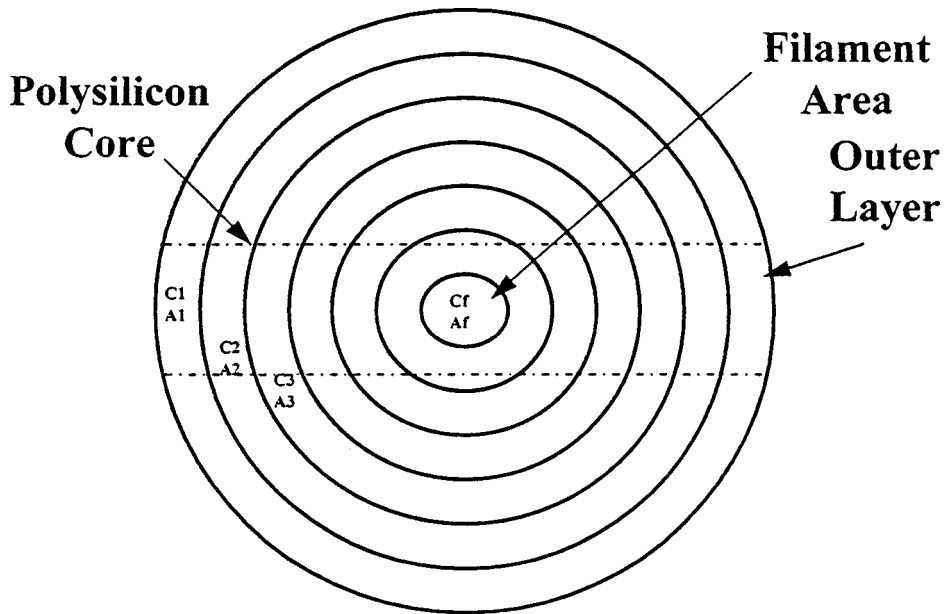


FIG. 5 Polysilicon Rod Cross Section

Concentration (Volume Averaged Calculation)

$$= \frac{(A1C1 + A2C2 + \dots + AfCf)}{(A1 + A2 + \dots + Af)}$$

where:

- $A1, A2, Af$ = corresponding area of poly rod cross section (see Fig. 5), and
- $C1, C2, Cf$ = concentration of impurity at corresponding area, corrected for segregation factor. For phosphorus, the measured value is divided by the segregation factor shown above.

13.3.3 To calculate volume averaged phosphorus values from the resistivity data of 12.6.3.1, determine the net compensated donor concentration according to:

$$\text{Netcompensated donor concentration (ppba)} = \frac{85}{\text{resistivity, (ohm-cm)}} (P \text{ ppba} + As \text{ ppba} - B \text{ ppba} - Al \text{ ppba})$$

13.3.3.1 Determine boron, arsenic, and aluminum values from the photoluminescence or FT-IR spectra, and use these values and resistivity data to calculate the P value in the above equation for the volume averaged calculation.

13.3.4 *Carbon Calculation*—Carbon values, analyzed as described in 12.6.3.3, are calculated according to the procedure described in 13.2.

14. Precision and Bias

14.1 In Section 11, the use of control rod samples to monitor interfering impurity levels in the sample preparation, etch procedure, and zoner furnace was discussed. Data was collected for 156 control rods, zoned in three different growth furnaces, over a 1-year period. Results are shown in Table 1. All samples were etched by the same procedure, using freshly prepared acid for each etch bath. Boron and phosphorus values were measured by photoluminescence spectroscopy. Carbon values were measured by cryogenic FTIR spectroscopy. Boron was measured at 6-zone lengths of the ingot, phosphorus at 12-zone lengths, and carbon at 12-zone lengths. Precision for the boron and phosphorus measurement, as two sigma, is stated in Method F 1389 as 0.002 ppba. Precision for the carbon

TABLE 1 Control Rod Analysis Using 3 Zoners

	Zoner 1		Zoner 2		Zoner 3	
	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.
Phosphorus (ppba)	0.011	0.007	0.010	0.010	0.010	0.004
Boron (ppba)	0.008	0.006	0.006	0.006	0.009	0.006
Carbon (ppma)	0.06	0.03	0.05	0.05	0.06	0.03

measurement for Method F 1391 is stated as 0.02 ppma.

14.2 To compare sample preparation, etching techniques, and zoning techniques between different laboratories, polysilicon rod sections were cut from one large polysilicon

rod and the sections sent to three different laboratories. Following the procedures outlined in this practice, each laboratory prepared, etched, and zoned its own samples, using different diameters. Each laboratory zoned the ingots in one pass in argon then prepared the samples for photoluminescence analysis. Data is shown in Table 2.

TABLE 2 Comparison of Zoned Ingots

	Boron (ppba)	Phosphorus (ppba)
Laboratory A	0.008	0.008
Laboratory B	0.007	0.010
Laboratory C	0.012	0.013

15. Keywords

15.1 contaminants; float-zone crystal growth; impurities; polycrystalline silicon; polysilicon evaluation; segregation coefficient; single crystal silicon

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