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Standard Practice for Evaluation of Granular Polysilicon by Melter-Zoner Spectroscopies[1]

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1. Scope

1.1 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.

1.2 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 0.03 to 5 parts per million atomic (ppma) for carbon. The acceptor and donor impurities are analyzed in a slice taken from the single crystal ingot by photoluminescence or infrared spectroscopies. The carbon impurity is determined by analysis of a slice by infrared spectroscopy.

1.3 This practice is applicable only to evaluation of polysilicon granules as produced by thermal deposition of silane, or one of the chlorosilanes, onto high purity seeds of polysilicon in a continuous fluid bed reactor. The granules are near spherical in shape and range in size from 200 to 2500 µm with a mean size of about 900 µm.

1.4 *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.* Specific hazard statements are given in Section 9 and in 12.1.1.

2. Referenced Documents

2.1 ASTM Standards:

D 5127 Guide for Electronic Grade Water[2]
F 1241 Terminology of Silicon Technology[3]
F 1389 Test Methods for Photoluminescence Analysis of Single Crystal Silicon for III-V Impurities[3]
F 1391 Test Method for Substitutional Atomic 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 SEMI Standards:

Specification for Gases[4]
Specification for Process Chemicals[4]

3. Terminology

3.1 Most terms used in this practice are defined in Terminology F 1241.

3.2 *Definitions of Terms Specific to This Practice:*

3.2.1 *granular polysilicon, n*—nearly spherical, granules (200 to 2500 µm) of polysilicon as produced in a fluidized bed reactor.

3.2.2 *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.

3.2.3 *PTFE*—an acronym for polytetrafluoroethylene, a chemically resistant polymer.

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

4. Summary of Practices

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

4.1.1 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 12 g of polysilicon has been melted and cooled in the zone process, a polysilicon rod about 0.9 by 6 cm is obtained.

4.1.2 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 0.9 cm in diameter by 5 cm in length from which a section is sliced for measurement of impurities. The entire consolidation and zoning requires about 30 min to accomplish.

4.1.3 A slice of 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.

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

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

[4] Available from Semiconductor Equipment and Materials International, 805 E. Middlefield Rd., Mountain View, CA 94043.

5. Significance and Use

5.1 Polycrystalline silicon is used as the starting material for growth of large single crystal ingots by the Czochralski methods. This procedure provides a means to determine the impurity levels in granular polysilicon to be used for crystal growth.

5.2 Although the 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.

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

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

6. Interferences

6.1 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 the polysilicon.

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

6.3 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.

7. Apparatus

7.1 *Acid Exhaust Fume Hood*, a hood which can provide for exhaust of acid fumes, provide a clean air environment (Class 1000 minimum), a drain for acids and water, and supplied with deionized water. 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.

7.2 *Laminar Flow Hood*, a hood which will provide a flow of clean (Class 1000 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 55.6 cm. 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 Fig. 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 setup and utilized inside a Class 1000 clean room.

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.

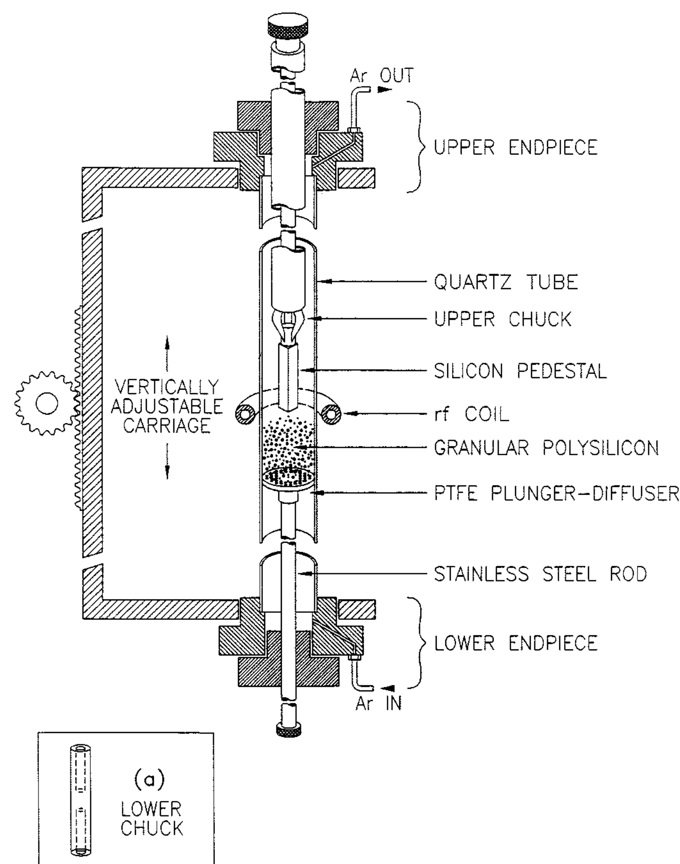

FIG. 1 Melter/Float Zone Apparatus

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 Fig. 1). This will support 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 8-cm rod.

7.9 *Hydrogen Torch*, is 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 of 2 to 4-mm thick from the single crystal ingot.

8. Reagents and Materials

8.1 *Hydrogen Gas*, low purity gas cylinder for hydrogen torch.

8.2 *Argon Gas*, in accordance with SEMI Specification C 3.14.

8.3 *Hydrofluoric (HF) Acid (49 %)*, in accordance with SEMI Specification C 1.8.

8.4 *Nitric (HNO_3) Acid (70 %)*, in accordance with SEMI Specification C 1.12.

8.5 *Mixed Acid Etchant (MAE) 57:18:25*, composed of HNO_3:HF:Acetic Acid, in accordance with SEMI C2.1.

8.6 *Methanol*, in accordance with SEMI C1.10.

8.7 *Deionized (DI) Water*, electronic grade Type E-2 as described in Guide D 5127.

8.8 *Clean Room Garb*, including gowns, gloves, lint free paper, etc.

8.9 *Polyethylene Forceps*, size to hold 6 to 12-mm silicon slice.

8.10 *PTFE Beakers*, 100 mL in size for handling acids used in etching or cleaning.

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

8.12 *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-kg specially lined drums), or at the point of use. The sampling point is therefore determined by the purpose of the evaluation.

11. Reference Specimens

11.1 A large homogeneous sample of granular polysilicon reference material is used to monitor the process of consolidation and conversion to a single crystal silicon. This reference material is periodically and repeatedly converted to single crystal silicon to establish the consistency and cleanliness of this practice.

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

12. Preparation of Apparatus

12.1 Cleanliness of all parts of the melter/zoner, especially the quartz tube, sample containers, transfer funnel, and the carriage endpieces is of utmost concern.

12.1.1 The inner part of the quartz tube is cleaned and etched with 3:1 HF:HNO_3.

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. Following the acid etch, the tube is rinsed with copious amounts of DI water and allowed to dry in laminar air flow hood.

12.1.2 Other quartz parts, including sample containers and funnels, are etched clean and dried as in 12.1.1 except the etchant is 1:1 HF:H_2O.

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

12.2 The silicon pedestals and single crystal seed rods are prepared 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 1—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 10 to 12 cm below the rf coil. Start the argon purge and diffuser gas flow at a rate of about 0.1 SCFM, standard cubic feet per minute 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 until the upper bed of granules is near the lower part of the rf coil; about 25 g of polysilicon is needed. 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 3 cm 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 2—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 6 cm 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 Fig. 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 3—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 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, use Test Method F 1391, an infrared spectrophotometric analysis. For determination of donor and acceptor contents, use either one or both of the following test methods: Test Method F 1630, a low-temperature FT-IR analysis, or Test Method F 1389, a photoluminescence analysis.

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 *Precision*—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.

16. Keywords

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

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