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DIN 50434

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Crystallographic Perfection of Silicon by Preferential Etch Techniques[1]

This standard is issued under the fixed designation F 47; 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 test method is valid, but limited in scope and application. A series of task forces has been established within F 1.06 Section D, to enhance and expand the applicability of this and other related documents. When the new test method is approved, this test method will be withdrawn.

1. Scope

1.1 This test method[2] is used to determine whether an ingot or piece of silicon is monocrystalline in structure and if so, the density of dislocations which may be present. Swirls and striations may also be delineated. These crystal defects are described to avoid confusion when counting dislocation etch pits.

NOTE 1—Test Method F 416, although destructive, is preferred for detection of oxidation induced defects.

1.2 This procedure is suitable for silicon crystals with dislocation densities between 0 and 100 000 cm^{-2}.

1.3 Silicon crystals doped either *p* or *n* type and with resistivities as low as 0.005 Ω·cm may be evaluated. This test method is applicable for evaluation of silicon crystals grown in either a [111] or a [100] direction.

1.4 This test method utilizes a chemical preferential etchant to delineate crystallographic defects. Two etchants are included, Sirtl etch for [111] silicon (9.4.1), and the Schimmel etch for [100] silicon (9.4.2). While the Sirtl etch usage is limited to [111] silicon, the Schimmel etch can be used for silicon crystals grown in both [100] and [111] directions.

NOTE 2—DIN 50434 differs from this test method in that it does not include procedures for (100) silicon, it provides a four-digit numerical classification of surface quality, and it uses a slightly different procedure for counting the number of dislocations.

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.* Specific hazard and hazard statements are given in Section 10.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[3]

E 7 Terminology Relating to Metallography[4]

F 26 Test Methods for Determining the Orientation of a Semiconductive Single Crystal[5]

F 416 Test Method for Detection of Oxidation Induced Defects in Polished Silicon Wafers[5]

2.2 *American National Standard:*

B74.10 Specification for Grading of Abrasive Microgrits[6]

2.3 *SEMI Standard:*

C1 Specifications for Reagents[7]

3. Terminology

3.1 *Definitions:*

3.1.1 The following are definitions of crystallographic terms which have particular meaning in the semiconductor industry for silicon crystals:

3.1.1.1 *crystal*—a solid composed of atoms, ions, or molecules arranged in a pattern which is periodic in three dimensions.

3.1.1.2 *dislocation*—a line imperfection in a crystal which possesses certain specific characteristics. This type of crystal imperfection **(1, 2)**[8] is either a line imperfection which forms the boundary between the slipped and nonslipped areas of a crystal, or a line imperfection which is characterized by a closure failure of Burger's circuit.

3.1.1.3 *grain boundary*—the surface, which may be closed, over which a crystal is in contact with other crystals in a solid body. Any point on this surface or interface constitutes the junction of at least two differently oriented crystal lattices. For polycrystalline material, this orientation

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

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[2] DIN 50434 is an equivalent method. It is the responsibility of DIN Committee NMP 221, with which Committee F-1 maintains close technical liaison. DIN 50434, Testing of Inorganic Semiconductor Materials: Determining the Crystalline Imperfections of Monocrystalline Silicon Specimens on Etched [111] Surfaces, is available from Beuth Verlag GmbH Burggrafenstrasse 4-10, D-1000 Berlin 30, Federal Republic of Germany (see also Vol 10.05).

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

[4] *Annual Book of ASTM Standards*, Vol 03.01.

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

[6] Available from American National Standards Institute, 11 West 42nd St., 13th Floor, New York, NY 10036.

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

[8] Boldface numbers in parentheses refer to references at the end of this test method.

difference is appreciable (greater than 1.0 min of arc), and the boundary is a large-angle boundary. When this orientation difference is very small, the boundary is a subboundary or a low-angle boundary known as lineage (3.1.1.4).

3.1.1.4 *lineage*—a low-angle grain boundary resulting from an array of dislocations.

DISCUSSION—The difference in orientation across the grain boundary may vary from a fraction of a second to a minute of arc. The array of dislocations appears as a row of pits on a preferentially etched surface.

3.1.1.5 *polycrystalline*—a form of semiconductor material made up of randomly oriented crystallites and containing large-angle grain boundaries, twin boundaries or both.

3.1.1.6 *single crystal* (*monocrystal*)—a body of crystalline material which contains no large-angle grain boundaries or twin boundaries.

3.1.1.7 *slip—in semiconductor wafers*, a process of plastic deformation in which one part of a crystal undergoes a shear displacement relative to another in a fashion that preserves the crystallinity of the material.

DISCUSSION—After preferential etching, slip is evidenced by a pattern of one or more parallel straight lines of dislocation pits that do not necessarily touch each other. On {111} surfaces, groups of lines are inclined at 60° to each other; on {100} surfaces, they are inclined at 90° to each other.

3.1.1.8 *striations—in semiconductor technology*, helical features on the surface of a silicon wafer associated with local variations in impurity concentration.

DISCUSSION—Such variations are ascribed to periodic dopant-incorporation differences occurring at the rotating solid-liquid interface during crystal growth. These features are visible to the unaided eye after preferential etching and appear to be continuous under 100× magnification.

3.1.1.9 *swirl*—helical or concentric features that are visible to the unaided eye after preferential etch, and appear to be discontinuous under 100× magnification.

3.1.1.10 *twin band*—a volume within a crystal bounded by twinning planes.

3.1.1.11 *twinned crystal*—a crystal in which the lattice is of two parts related to each other in orientation as mirror images across a coherent planar interface, known as the twinning plane or twin boundary.

DISCUSSION—In a diamond cubic crystal, such as silicon, this plane is a {111} plane.

3.1.2 Definitions of general terms related to crystallography may be found in Terminology E 7.

4. Summary of Test Method

4.1 The end portion of the silicon crystal which solidified last (tang end) is immersed in the defect etchant solution. This crystal area normally has many dislocations which are indicated by etch pits. The portion containing the dislocation etch pits is cropped off. A specimen slice is cut from the remaining ingot adjacent to the cropping location, mechanically and chemically polished, and then etched in the defect etchant solution. The etched surface is examined microscopically to reveal the nature and extent of crystal imperfections.

5. Significance and Use

5.1 The use of crystals in many semiconductor devices requires a consistent atomic lattice structure. Variations (crystal imperfections) locally disturb the energy conditions which are the basis for semiconductor behavior (**3**), and have distinct effects on essential semiconductor device manufacturing processes such as alloying and diffusion.

5.2 This test method may be used for process control, research and development, and materials acceptance purposes.

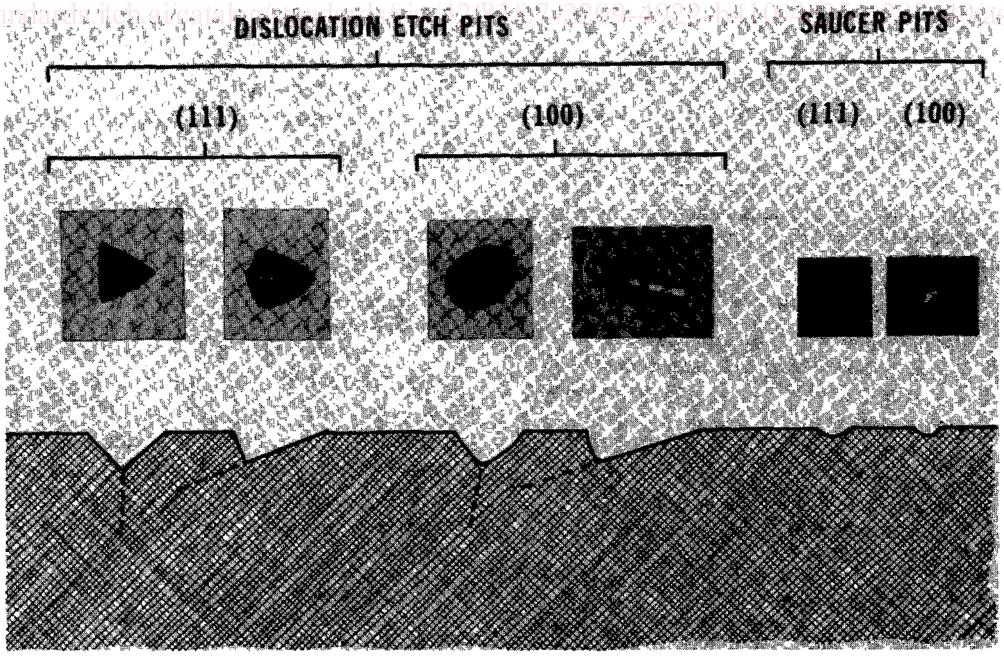
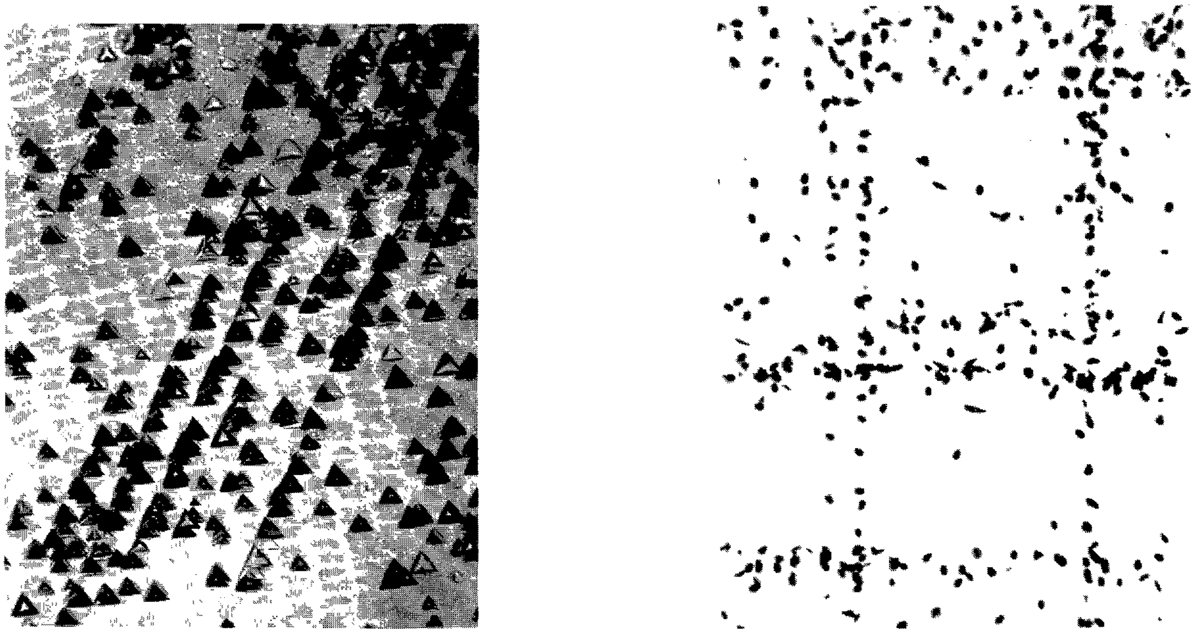


FIG. 1 Typical Dislocations and Saucer Pits for (100) and (111) Etched Surfaces



(a) (111) Silicon Slice

(b) (100) Silicon Slice

FIG. 2 Slip Dislocation Etch Pits

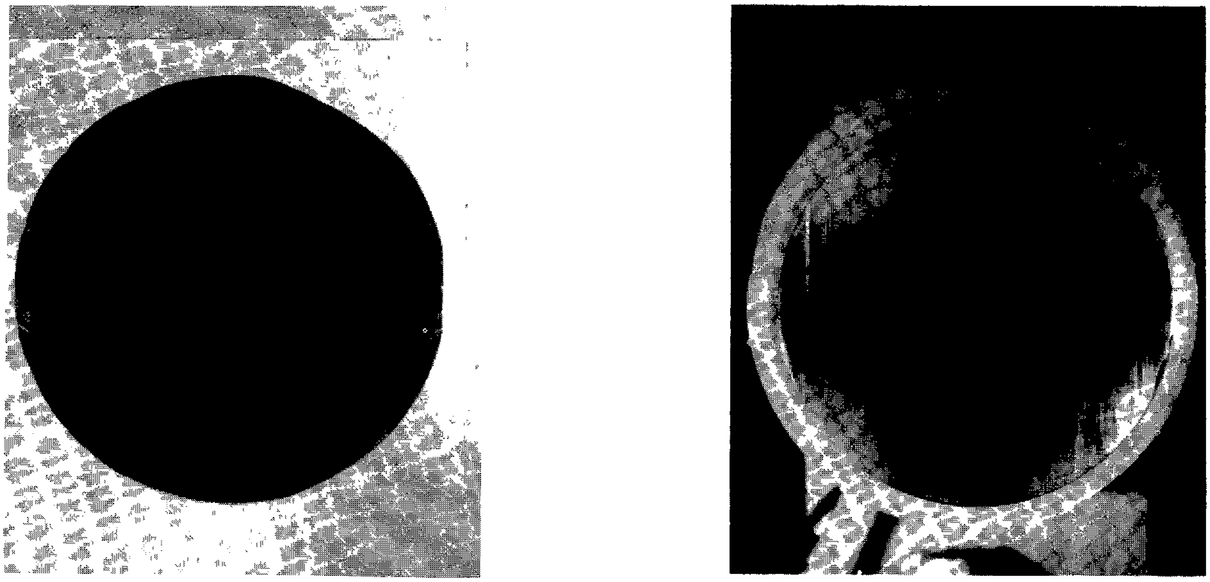
6. Characteristics of Revealed Imperfections

6.1 When a silicon specimen is evaluated by the specific etch compositions described in this test method, certain of the phenomena defined in 5.1 are characterized by the resulting patterns of the etched surface:

6.1.1 Typical examples of etch pits are shown in Fig. 1.

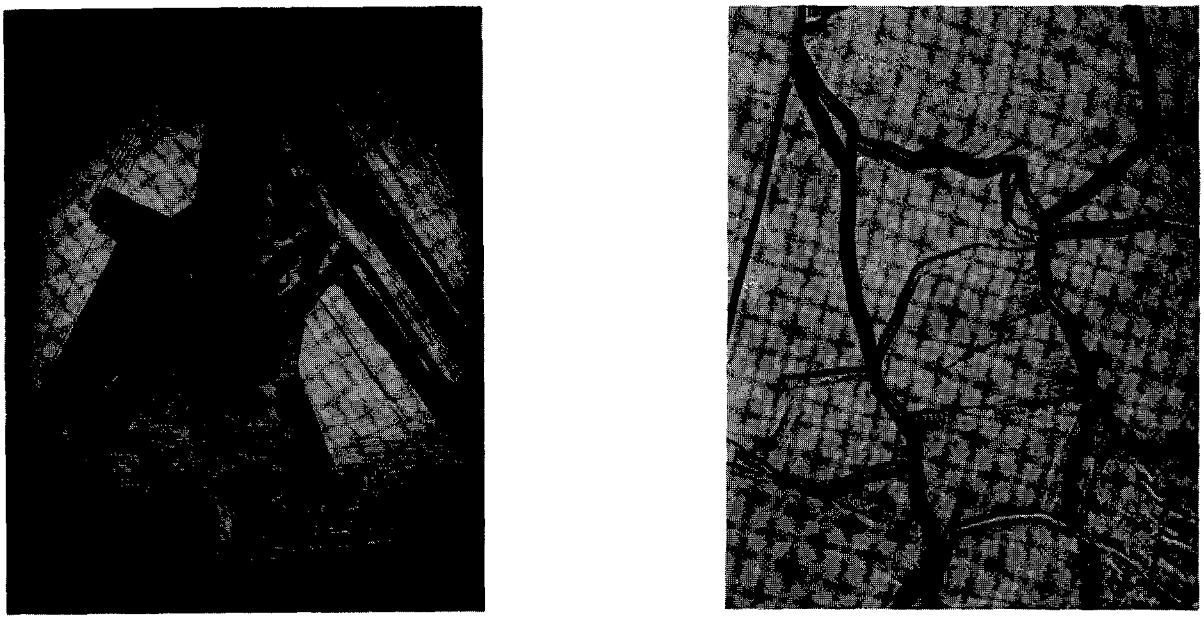
6.1.1.1 Dislocations on (100) surfaces etched with Schimmel etch (see 9.4.2) are characterized by microscopic etch pits whose shape varies from circular to elliptical, due to the isotropic nature of the etchant. The circular shape is associated with dislocations which intercept the surface at an angle of 90°, while the elliptical etch pits depict dislocations intercepting the surface at less than 90°. Saucer pits are similar in appearance to dislocation etch pits except that they are smaller and shallower and have more rounded bottoms.

6.1.1.2 Dislocations on (111) surfaces etched with Sirtl etch (see 9.4.1) are characterized by microscopic etch pits with approximately triangular sides and pointed bottoms. However, the triangular shape will be skewed for dislocations which intercept the surface at angles less than 90°. Saucer pits



(b) (100) Silicon Slice

FIG. 3 Surface of Entire Silicon Slice Indicating Slip



(a) Polycrystalline Region

(b) Grain Boundary

FIG. 4 Silicon Surfaces After Etching

are similar in appearance to dislocation etch pits except that they are smaller and shallower and have more rounded bottoms.

NOTE 3—Dislocations and saucer pits on (111) surfaces etched with Schimmel etch are similar in character to those on (100) surfaces due to the isotropic nature of the etchant.

6.1.2 Slip in a silicon wafer is evidenced by a pattern of one or more straight lines of dislocation etch pits which do not necessarily touch one another. The lines of etch pits will be in $\langle 110 \rangle$ directions.

6.1.2.1 The bases of the triangular slip dislocation etch pits for a (111) surface will be on a common line, see Fig. 2(*a*). Often the array of pits on a (111) surface covers the entire cross section of the crystal and appears to the unaided eye as a triangle or six pointed star, see Fig. 3(*a*).

6.1.2.2 The slip dislocation etch pits for a (100) surface will be in the semblance of straight lines, see Fig. 2(*b*). Often

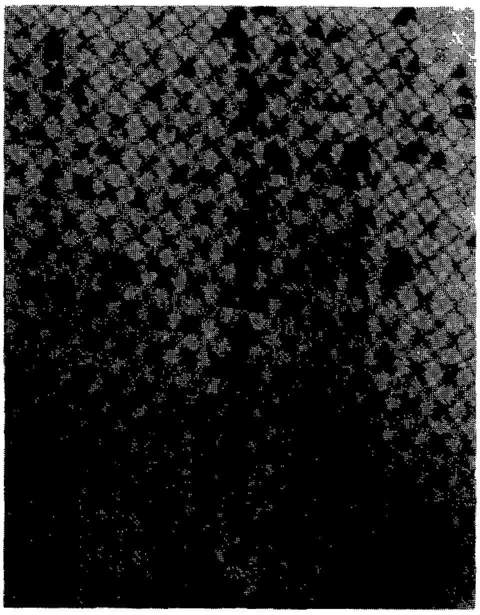
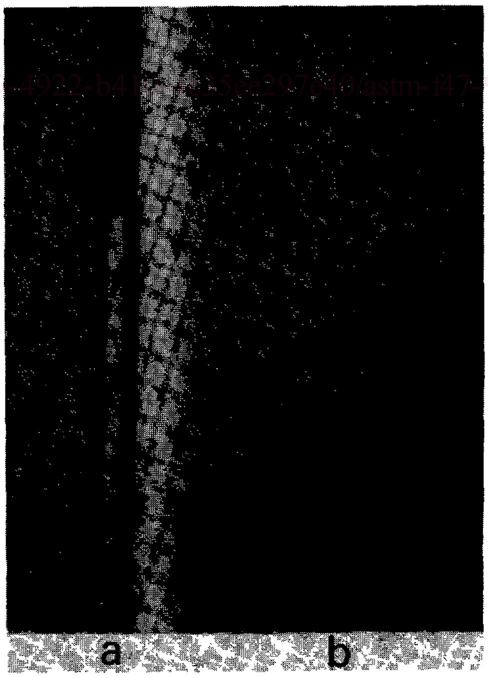
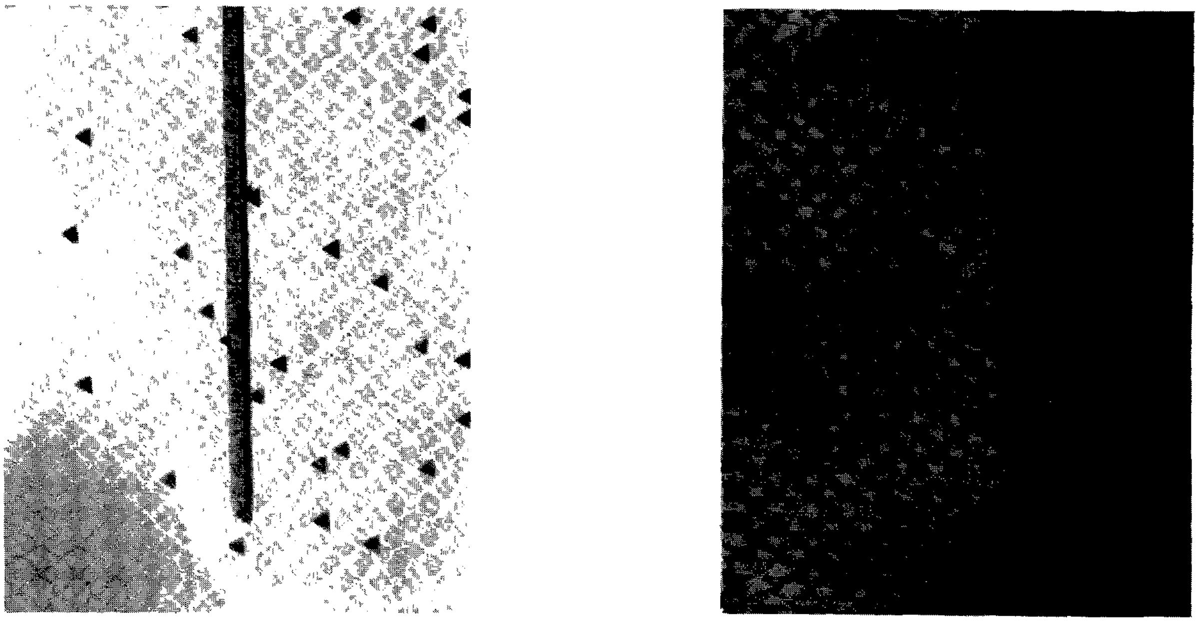


FIG. 5 Lineage on (111) Silicon Surface



(a) Twin Lamella
(b) Twin Boundaries

FIG. 6 Twin Lamella and Twin Boundaries of (100) Silicon Surface



(*a*) Twin Lamella

(*b*) Twin Boundary

FIG. 7 Twin Lamella and Twin Boundary at (111) Silicon Surface

the array of pits on a (100) surface covers the entire cross section of the crystal and appears to the unaided eye as straight lines from the slice edge or a square, see Fig. 3(*b*).

6.1.3 Polycrystalline material appears as a mosaic etch pattern to the unaided eye under strong illumination, see Fig. 4(*a*) (an area of polycrystalline material in a (111) silicon sample).

6.1.4 A grain boundary appears as a grooved line of any length in which individual dislocation etch pits cannot be resolved microscopically at a 200× magnification, see Fig. 4(*b*). In polycrystalline material the grooved lines enclose an area of the etched surface or extend to the periphery of the specimen.

6.1.5 Lineage on (111) surfaces appears as a linear array of dislocation etch pits with a linear density greater than 25 pits/mm. The individual dislocation etch pits on (111) surfaces are aligned point to base, see Fig. 5. However, lineage on (100) surfaces is indistinguishable from slip. For this test method, linear arrays less than 0.5 mm in length are not considered lineage.

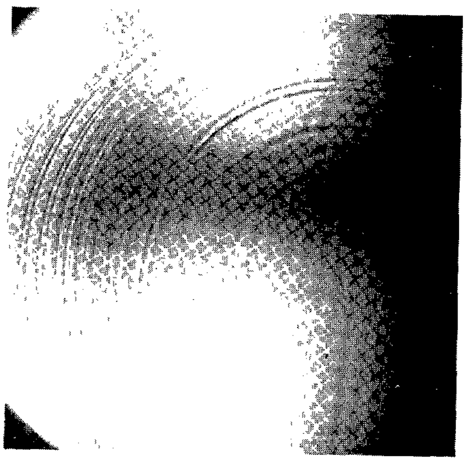


FIG. 8 Striations on (111) or (100) Silicon Surface

6.1.6 A twin boundary appears as a straight line at the intersection of a (111) plane and the etched surface being examined, see Figs. 6(*b*) and 7(*b*). Two parallel twin boundaries that are separated by only a few crystal lattice planes form a twin lamella which appears as a straight grooved line, see Figs. 6(*a*) and 7(*a*).

6.1.7 Under strong illumination, see Fig. 8, striations are evidenced by an etch pattern of a series of concentric rings to the unaided eye. These etch features are continuous at approximately a 150× magnification or greater.

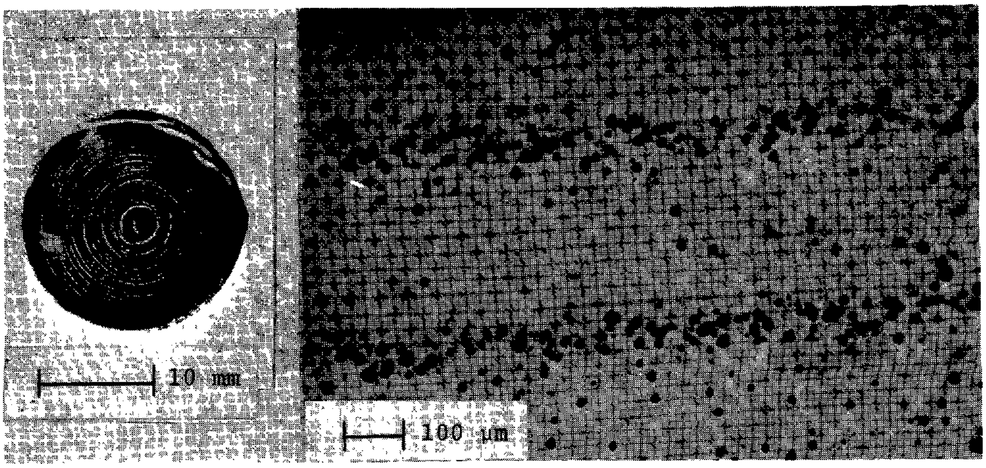
6.1.8 Under strong illumination, swirls are evidenced by a helical etch pattern to the unaided eye, see Fig. 9(*a*). However, at a magnification of 100×, or greater, the etch feature is composed of discrete etch pits, principally saucer pits, see Fig. 1 and 9(*b*). However, the presence of saucer pits is not unique to swirl defects.

7. Interferences

7.1 Identification of structures as revealed or enhanced by any of the etching techniques described in this test method must be made carefully. Unless care is exercised, identification of the defect structure may be ambiguous and result in significant counting errors of dislocation etch pits.

7.1.1 Etch artifacts are the primary cause of difficulty in identifying dislocation etch pits. Etch artifacts are generated in various ways such as gas bubble formation during etching, improperly cleaned surface prior to etching, or insufficient etch solution volume.

7.1.2 Excessive silicon staining (very dark color) either from the chemical polish etch or during the preferential etching may obscure or prevent the development of dislocation etch pits.



(*a*) On (111) or (100) Silicon Surface

(*b*) Saucer Pits of Swirl Pattern

FIG. 9 Swirl Patterns

7.1.3 The use of ultrasonic agitation may cause surface damage which can result in etch artifacts and erroneous etch pit results.

7.2 When dislocation etch pit counts or densities are to be compared with results of others, it is imperative that the same magnification be used, as well as the same shape (that is, circular, rectangular, or square) and area of the field of view.

7.3 Of equal importance for ensuring comparable etch pit counts and densities is the ability to locate precisely each of the nine specified counting locations with respect to the crystallographic orientation and starting point (see Fig. 10).

7.4 Care must also be taken to ensure that the line of travel of the sample specimen in the moving from one counting position to the next traverses the actual diameter of the wafer.

8. Apparatus

8.1 *Slicing Equipment*, suitable for removing slices for this test from ingots.

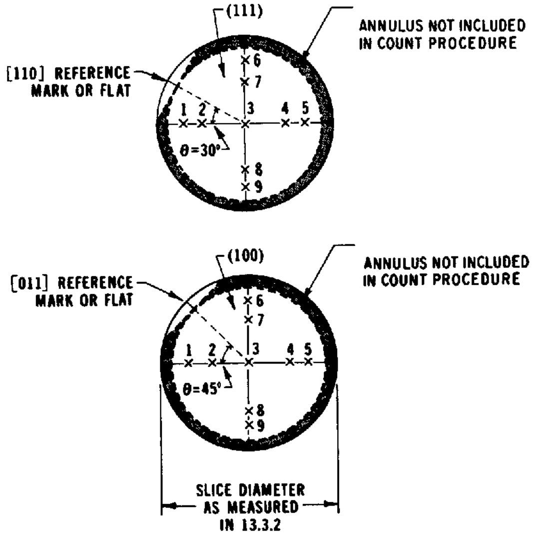


FIG. 10 Location of Count Positions on Slice Specimen

8.2 *Evaluation Equipment for Preparation and Examination of Metallographic Specimens*, including lapping facilities and a metallurgical microscope having an *X-Y* mechanical stage and a stage micrometer to calibrate the *X-Y* stage movement. The microscope shall preferably be equipped with interference contrast illumination and provided with 10×, 20×, and 40× magnifications objective lenses and 10× eye pieces.

8.3 *Stage Micrometer*, calibrated scale for length measurement in the form of a plate of glass or other suitable material on which graduations with a separation known to within the agreed upon uncertainty and at least as fine as the agreed upon value have been ruled or otherwise produced.

8.4 *Hydrofluoric Acid-Proof Chemical Laboratory Apparatus*, such as fluorocarbon, polyethylene, or polypropylene beakers, graduates, pipets, and tweezers.

8.5 *Acid Sink*, in a fume hood and facilities for disposing of acids and their vapors.

9. Reagents and Materials

9.1 *Purity of Reagents*—All chemicals for which such specifications exist shall conform to SEMI Specifications C1. Reagents for which SEMI specifications have not been developed shall conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society.[9] Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

9.2 *Purity of Water*—Reference to water shall be understood to mean either distilled water, or deionized water having a resistivity equal to or greater than Type II water as defined by Specification D 1193.

9.3 *Chemical Polish Etch*—A variety of useable formulations exists. The following have been found to produce

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[9] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.