Designation: F 1809 – 97

Standard Guide for Selection and Use of Etching Solutions to Delineate Structural Defects in Silicon [1]

This standard is issued under the fixed designation F 1809; 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.

1. Scope

1.1 This guide covers the formulation, selection, and use of chemical solutions developed to reveal structural defects in silicon wafers. Etching solutions identify crystal defects that adversely affect the circuit performance and yield of silicon devices. Sample preparation, temperature control, etching technique, and choice of etchant are all key factors in the successful use of an etching method. This guide provides information for several etching solution and allows the user to select according to the need. For further information see Appendix X1and Figs. 1-32 . For a test method for counting preferentially etched or decorated surface defects in silicon wafers see Test Method F 1810.

1.2 *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 Practice for Electronic Grade Water [2]

F 1725 Guide for Analysis of Crystallographic Perfection in Silicon Ingots [3]

F 1726 Guide for Analysis of Crystallographic Perfection in Silicon Wafers [3]

F 1727 Practice for Detection of Oxidation Induced Defects in Polished Silicon Wagers [3]

F 1810 Method for Counting Preferentially Etched or Decorated Surface Defects in Silicon Wafers [3]

2.2 *SEMI Specifications:*

SEMI C-1 Specification for Reagents [4]

3. Significance and Use

3.1 Structural defects formed in the bulk of a silicon wafer during its growth or induced by electronic device processing can affect the performance of the circuitry fabricated on that wafer. These defects take the form of dislocations, slip, stacking faults, shallow pits, or precipitates.

3.2 The exposure of the various defects found on or in a silicon wafer is often the first critical step in evaluating wafer quality or initiating failure analysis of an errant device structure. Etching often accomplishes this task.

4. Interferences

4.1 Complicating factors are different for each etchant. Research the choice of etchants in advance to ensure the

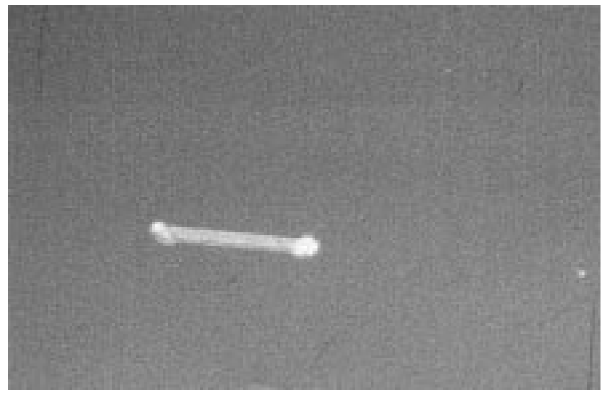

FIG. 1 Secco Etch With Agitation, Oxidation Stacking Fault, 1000x, [100], (1100°C Steam, 80 minutes), ~4 μm removal.

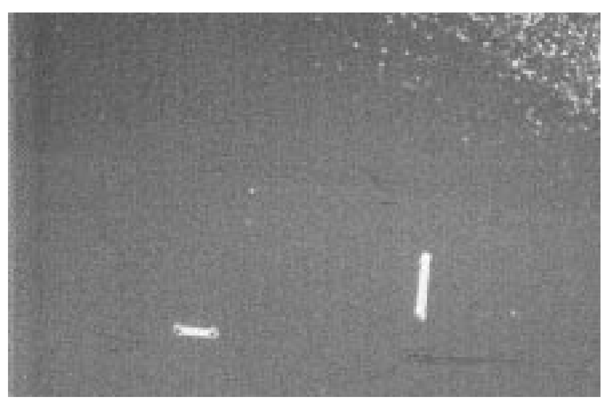

FIG. 2 Secco Etch With Agitation, Oxidation Stacking Fault, 400x, [100], (1100°C Steam, 80 minutes), ~4 μm removal.

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

Current edition approved June 10, 1997. Published August 1997.

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

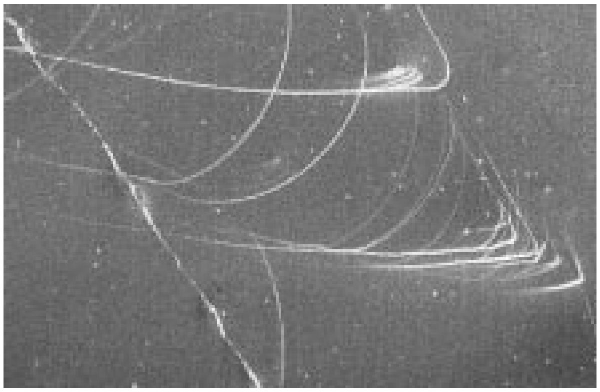

FIG. 3 Secco Etch Without Agitation, Flow Pattern Defect 200x, [100], ~8 μm removal.

FIG. 4 Secco Etch With Agitation, Expitaxial Stacking Fault, 150x, [100], ~4 μm removal.

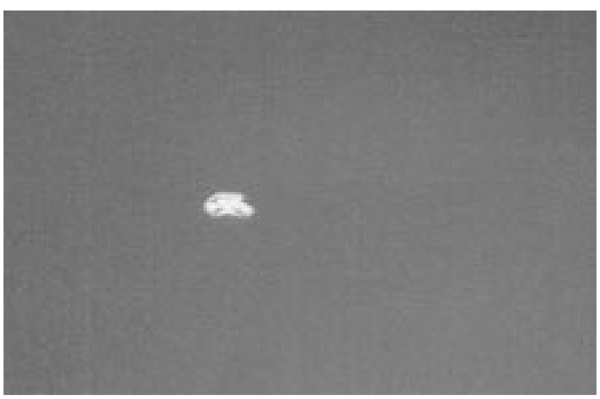

FIG. 5 Secco Etch With Agitation, Bulk Oxidation Stacking Fault, 200x, [100], (1100°C Steam, 80 minutes), ~15 μm removal.

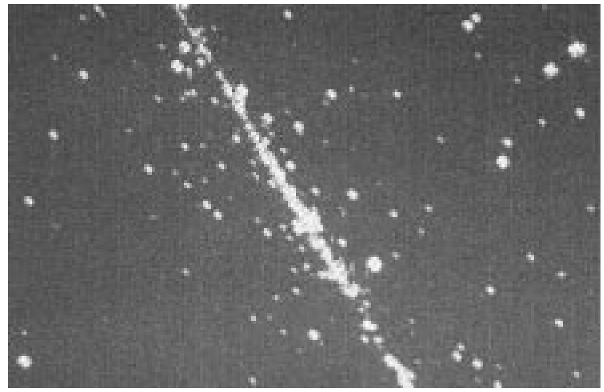

FIG. 6 Secco Etch With Agitation, Scratch Induced Oxidation Stacking Faults, 100x, [100], (1100°C Steam, 80 minutes), ~15 μm removal.

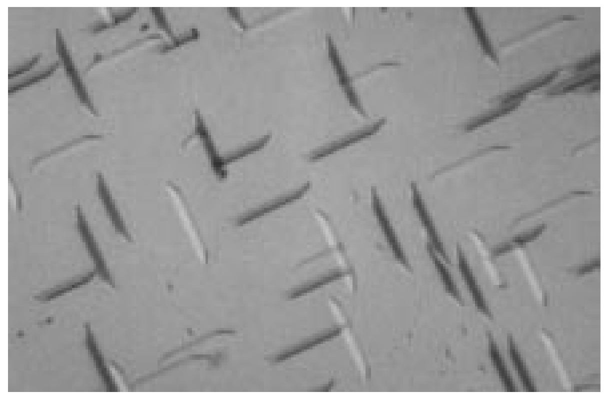

FIG. 7 Wright Etch With Agitation, Damaged Induced Oxidation Stacking Fault, 1000x, [100], (1100°C Steam, 80 minutes).

FIG. 8 Wright Etch With Agitation, Bulk Oxidation Stacking Fault, 500x, [100], (1100°C Steam, 80 minutes).

method and solution are compatible with the sample and objectives. Commonly encountered problems are:

4.1.1 Inadvertent etching through the denuded zone of an oxidized sample delineates irrelevant bulk defects instead of the surface oxidation induced stacking faults (OISF) expected.

4.1.2 Accelerated etching and etching artifacts can result from excessive solution heating during the etching process.

4.1.3 Insufficient agitation, bubble formation or particles in the etching solution can generate artifacts on the silicon surface that mimic actual defects. Insufficient agitation can alter the etching rate, increasing or decreasing it depending upon the formulation.

4.1.4 Any solution in which the oxidation rate is greater than the oxide dissolution rate may form oxide layers that slow or even quench the etching process. The presence of these oxide layers (especially for *N*+ and *P*+ material) obstructs the interpretation of etched defects. Before evaluation, remove any surface oxides.

4.1.5 The wafer surface becomes rougher with longer etch time. This rougher surface does not prevent evaluation under the microscope, but it greatly reduces the effectiveness of visual inspection under bright light.

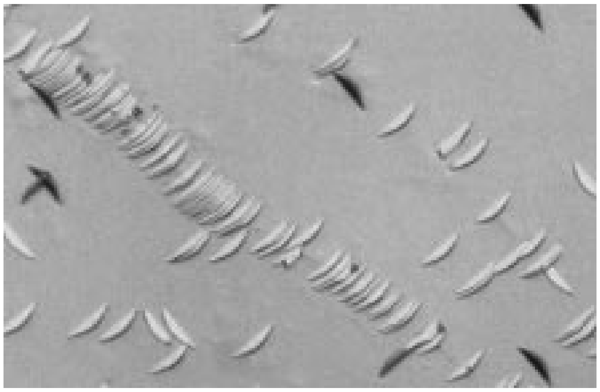

FIG. 9 Wright Etch With Agitation, Scratch Induced Oxidation Stacking Faults, 500x, Boron Doped [100], (1100°C Steam, 80 minutes).

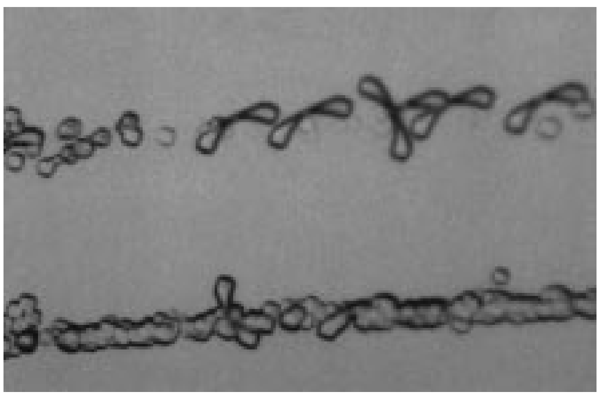

FIG. 10 Wright Etch With Agitation, Scratch Induced Oxidation Stacking Fault, 500x, Antimony Doped, [100], (1100°C Steam, 80 minutes).

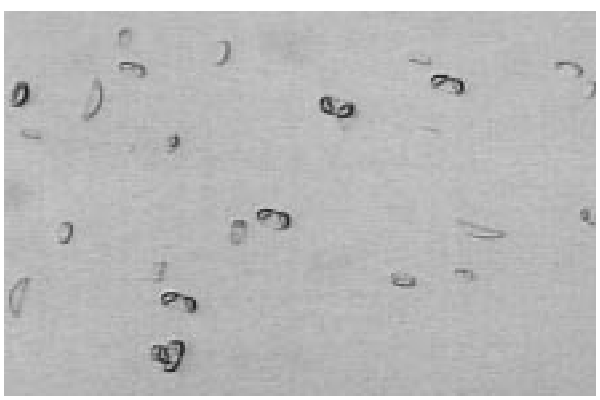

FIG. 11 Wright Etch With Agitation, Oxidation Stacking Fault, 500x, Low Resistivity Boron Doped, [100], (1100°C Steam, 80 minutes).

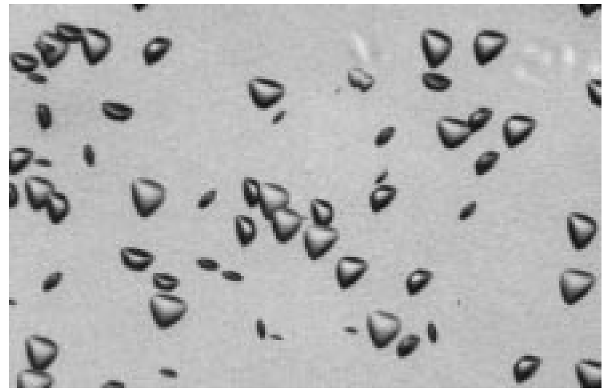

FIG. 12 Wright Etch With Agitation, Oxidation Induced Stacking Faults, 500x, [111], (1100°C Steam, 80 minutes).

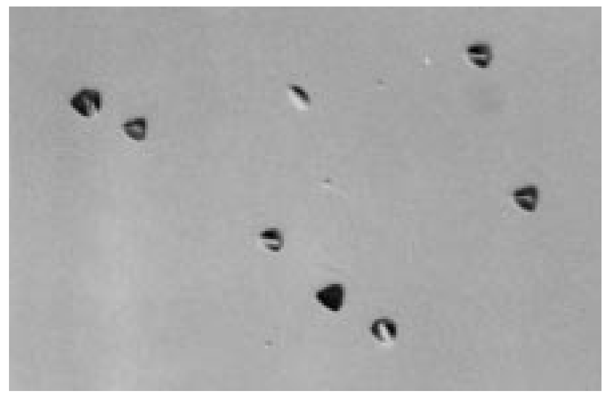

FIG. 13 Wright Etch With Agitation, Slip Dislocations, 500x, [111].

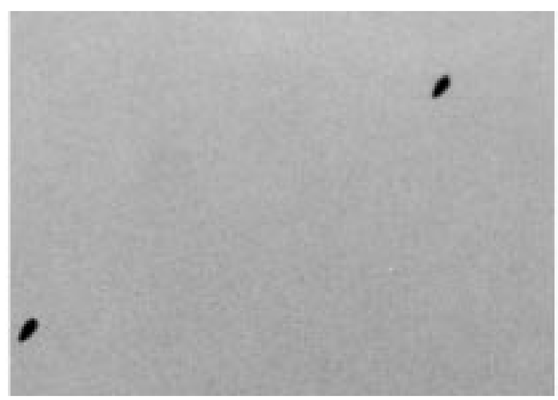

FIG. 14 Wright Etch With Agitation, Slip Dislocations, 200x, [100].

4.1.6 Etching solutions can generate false pits that are not associated with defects.

4.1.7 The samples must be free of work damage, contamination, and other complicating residues. Clean, specular surfaces are suitable for metallographic examination and provide the best results. Surfaces examined should be flat with parallel faces, to simplify microscope inspection.

5. Apparatus

5.1 No standard apparatus or facility satisfies the universal needs for the various etching solutions. Systems range from a simple beaker to large etching tanks complete with nitrogen bubblers, temperature control and nitrous oxide and hydrofluoric acid (HF) scrubbers.

5.1.1 For larger samples (wafers or slugs), use large etching tanks with nitrogen bubble agitation or ultrasonic agitation. Most of the etchant solutions listed work more effectively with the aid of agitation. Heat exchangers or just the thermal mass of the solution can control temperature. Large volumes of acid heat more slowly and allow an intrinsic form of temperature control. To reduce heating effects, maintain 1 L of solution for each 1 000 cm^2 of sample surface area.

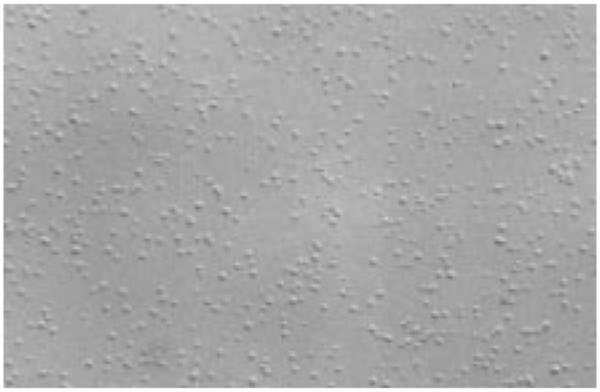

FIG. 15 Wright Etch With Agitation, Shallow Pits (Haze), 500x, Boron Doped [100], (1100°C Steam, 80 minutes).

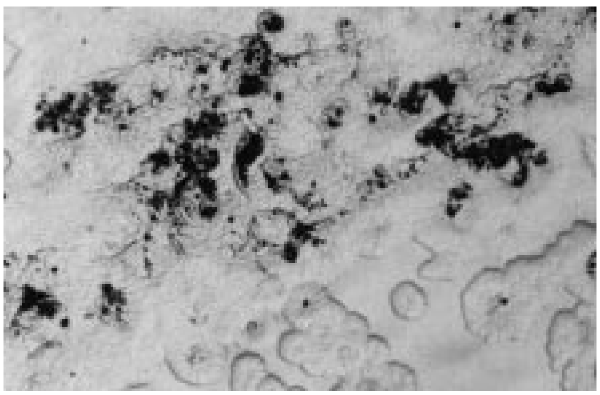

FIG. 16 Wright Etch, Etching Stain-Artifact, 200x, Boron Doped.

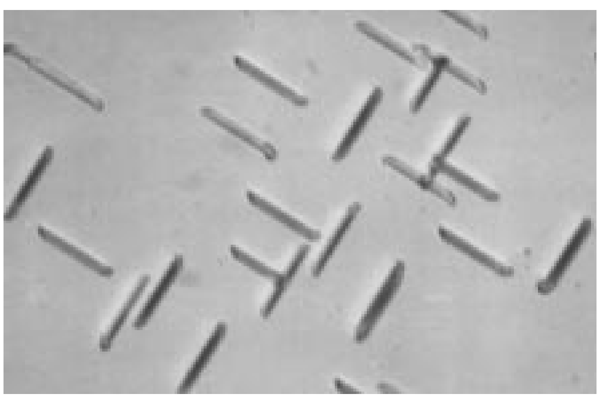

FIG. 17 Copper-3 Etch With Agitation, Oxidation Stacking Fault, 500x, p type, 10 ohm-cm, [100] (1100°C Steam, 80 minutes), 2 μm removal.

5.1.2 Maintain proper environmental controls. Make provisions to dispose of nitrous oxides, HF fumes, and any solid wastes evolved whatever system is chosen. Chromium and copper-based etching solutions produce solid waste and gaseous byproducts. Chromium-free etching solutions produce no measurable solid waste but do generate nitrous oxides and HF fumes.

6. Reagents and Materials

6.1 All chemicals for which such specifications exist shall conform to SEMI Specification C-1.

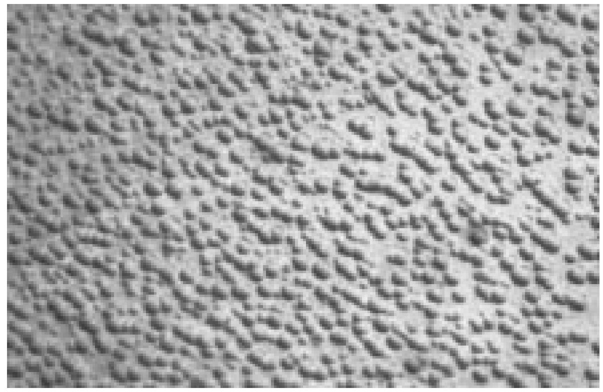

FIG. 18 Copper-3 Etch With Agitation, Shallow Pits (Haze), 500x, p type, 10 ohm-cm, [111], (1100°C Steam, 80 minutes), 2 μm removal

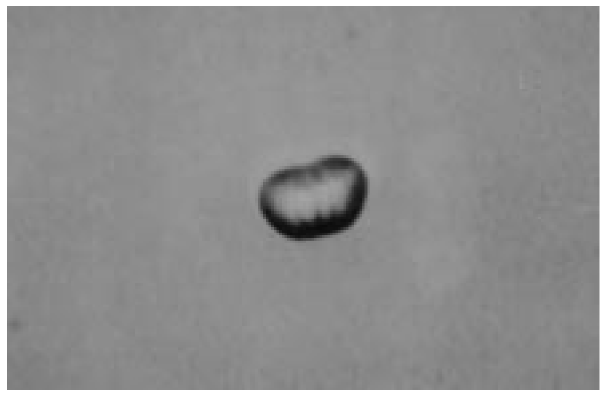

FIG. 19 Copper-3 Etch Without Agitation, Oxidation Stacking Fault, 1000x, p type, 10 ohm-cm, [111], (1100°C Steam, 80 minutes), 1 μm removal.

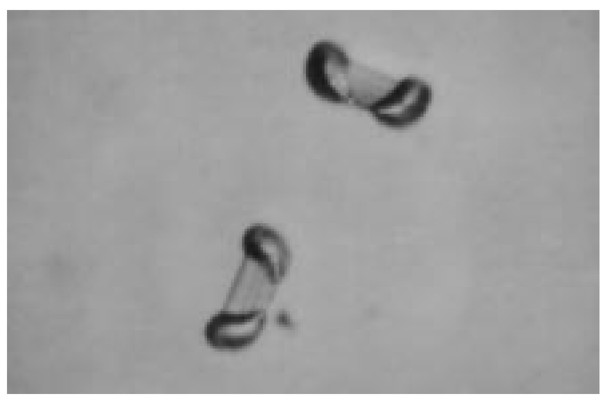

FIG. 20 Copper-3 Etch Without Agitation, Oxidation Stacking Fault, 1000x, p type, 10 ohm-cm, [100], (1100°C Steam, 80 minutes), 1 μm removal.

6.2 *Purity of Water*—Reference to water means either distilled or deionized water, meeting the requirements of Type I water as defined by Guide D 5127.

6.3 Volume of components describes all solutions in parts of a standard assay. The formulas give solid or dissolved components in grams per 100 mm of total solution.

6.4 All formulations employ a Standard Solution Convention (SSC) that specifies each solution component as an

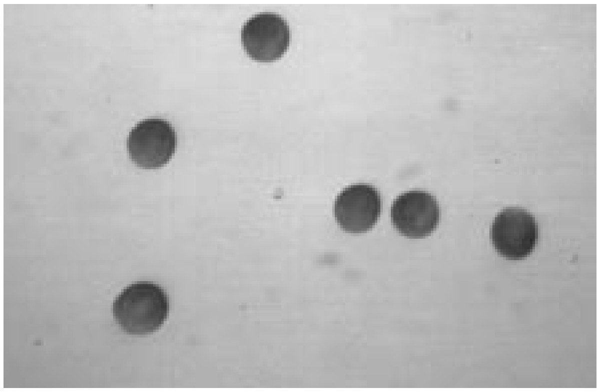

FIG. 21 Copper-3 Etch Without Agitation, Dislocations, 500x, p type, 10 ohm-cm [111], 10 µm removal.

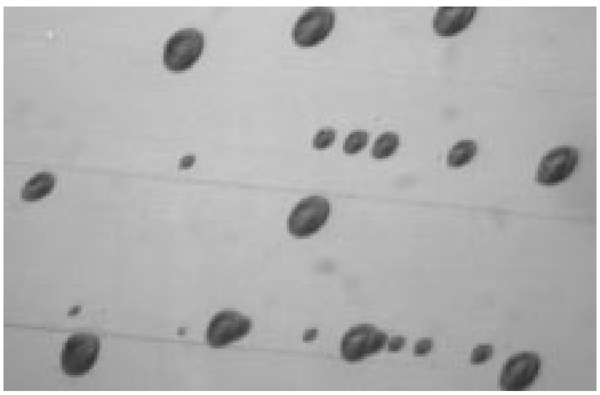

FIG. 22 Copper-3 Etch Without Agitation, Dislocations, 500x, p type, 10 ohm-cm, [100], 10 µm removal.

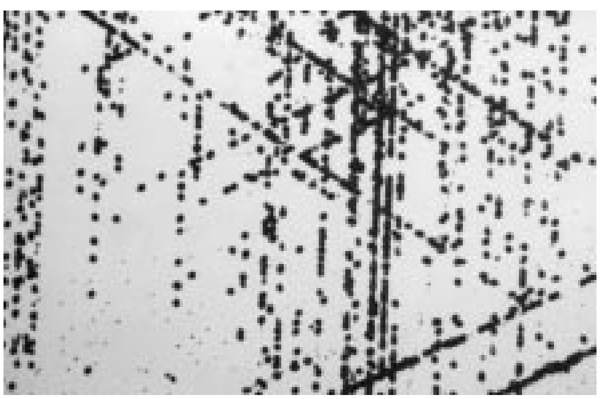

FIG. 23 Copper-3 Etch Without Agitation, Slip Dislocations, 100x, p type, 10 ohm-cm, [111], 10 µm removal.

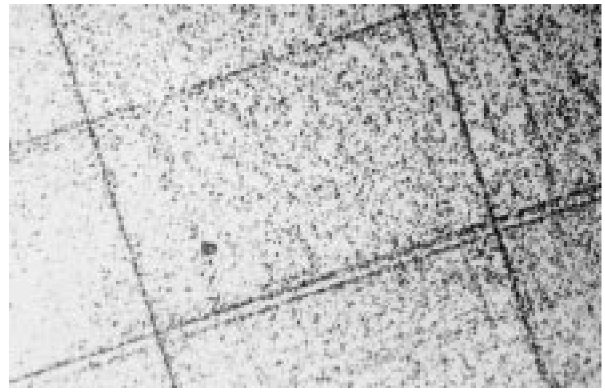

FIG. 24 Copper-3 Etch Without Agitation, Slip Dislocations, 100x, p type, 10 ohm-cm, [100], 10 µm removal.

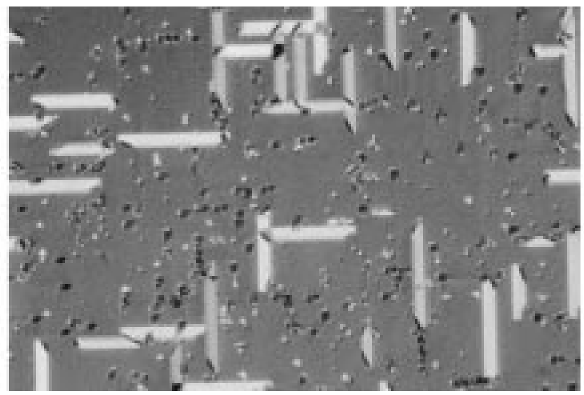

FIG. 25 Modified Dash Etch, Oxidation Induced Stacking Faults and Dislocations, 400x, [100], p type, 10 ohm-cm, (1100°C, O_2, 8 hour), ~4 µm removal.

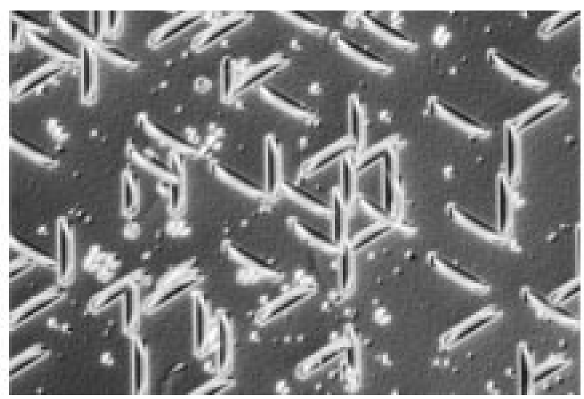

FIG. 26 Modified Dash Etch, Oxidation Induced Stacking Faults and Dislocations, 400x, [111], n type, 10 ohm-cm, (1100°C, O_2, 8 hour), ~4 µm removal.

acceptable assay ± some tolerance. Formulations of the standard assay follow this example: A HF/HNO_3/Acetic solution, in the 1:1:2 ratio is the same as 25 %(49 %HF) + 25 %(70 %HNO^3+ 50 %(glacial acetic) by volume. The specified chemicals shall have the following nominal assay:

Chemical	Assay, %
Acetic acid, glacial	> 99.7
Chromium trioxide	> 98
Copper nitrate	> 98
Hydrofluoric acid	49 ± 0.25
Nitric acid	70 to 71

7. Hazards

7.1 The chemicals used in these etching solutions are potentially harmful. Handle and use them in a chemical exhaust fume hood, with the utmost care.

7.2 Hydrofluoric acid solutions are particularly hazardous.

7.3 Release of chromic acid or solutions of chromic acid into domestic sewer systems is usually not allowed. Chromates are extreme biological and ecological hazards. Chromic acid is a strong oxidizing agent and should not contact organic solvents or other easily oxidized materials.

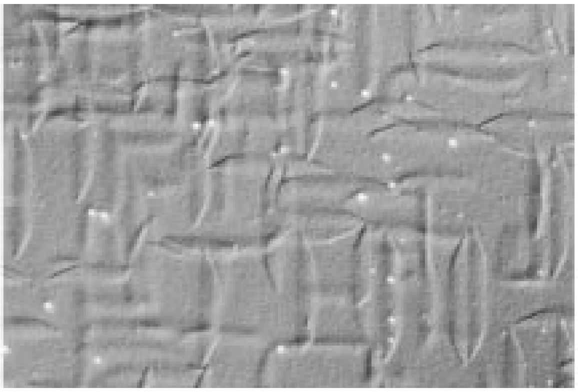

FIG. 27 Modified Dash Etch, Oxidation Induced Stacking Faults, 400x, [100], p type, 0.007 ohm-cm, (1100°C, O_2, 8 hour), ~5 µm removal.

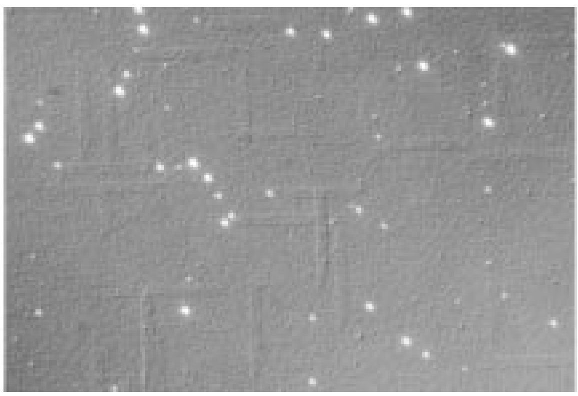

FIG. 28 Modified Dash Etch, Oxidation Induced Stacking Faults, 400x, [100], p type, <0.02 ohm-cm, (1100°C, O_2, 8 hour), ~5 µm removal.

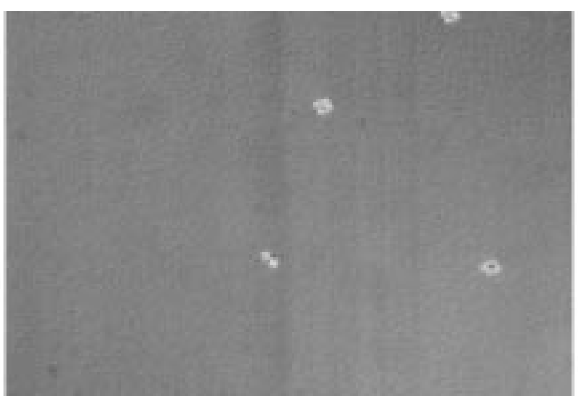

FIG. 29 Modified Dash Etch, Slip Dislocations p/p+ Epitaxy, 400x, [100], ~4 µm removal.

7.4 Safety or protective gear should be worn while handling these acid solutions or their components. Safety requirements vary, but the essentials are: plastic gloves, safety glasses, face shield, acid gown, and shoe covers. The handling of large quantities of powdered chromic acid may require a respirator or other breathing apparatus.

8. Procedure

8.1 *Selection of Etching Solutions*:

8.1.1 Table 1 and Table 2 contain a partial list of the many

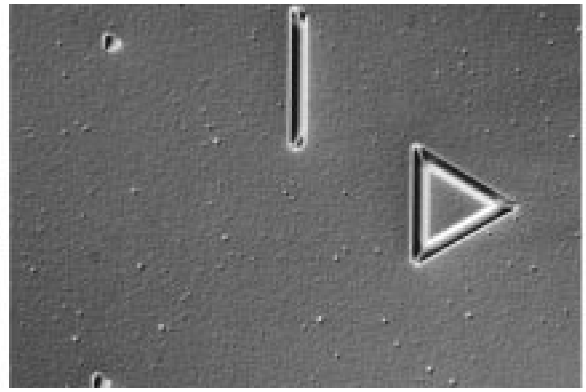

FIG. 30 Modified Dash Etch, Slip Dislocations, Epitaxial Stacking Faults and Shallow Pits, n/n+ Epitaxy, 400x, [111], ~4 µm removal.

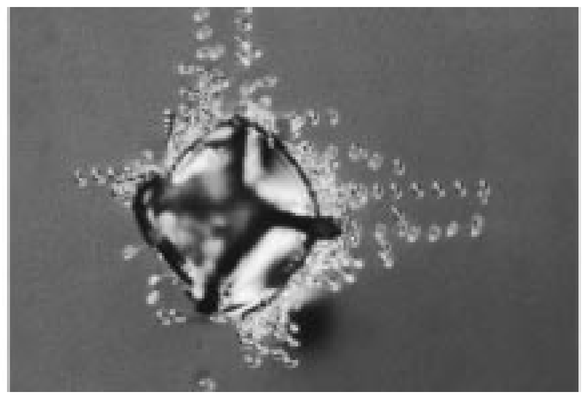

FIG. 31 Modified Dash Etch, Damage Induced Slip Dislocations, p type, 400x, [100], (1100°C, O_2, 1 min), ~4 µm removal.

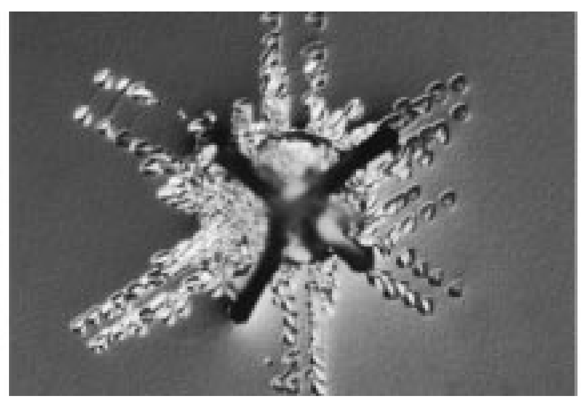

FIG. 32 Modified Dash Etch, Damage Induced Slip Dislocations, n type, 400x, [111], (1100°C, O_2, 1 min), ~4 µm removal.

published references and suggested applications. Each solution has advantages and disadvantages and this guide does not endorse one in favor of another. Selection of an etchant solution should be based upon: etch rate, etchant life, solution heating, environmental harm, ease of interpretation, and range of use.

NOTE 1—Although this guide does not require a specific solution, attempt to use chromium-free etches when possible for environmental reasons.

8.1.2 The following tables show two broad categories of solutions. The first, Table 1, is the group of solutions that contain chromium compounds. These do well for their intended application but can be harmful to the environment. Use these highly contaminated etching solutions with caution. Release into the environment of hexavalent chromium waste is a recognized hazard. Exposure can cause cancer. The second group inTable 2 lists the chromium-free etching solutions. Although uses may be limited, they should be considered whenever appropriate.

8.1.3 Investigate local environmental and safety requirements before selecting an etchant solution. Identify the sample orientation, type, resistivity level, and primary defects of interest; this information helps the user in ranking the various possible solutions and then in selecting the most appropriate choice.

NOTE 2—Flow pattern defects form a characteristic "*v*" shaped pattern when the wafer is etched in a vertical position without acid aggitation. Other applications of Secco etch require some form of agitation to avoid confusing artifacts associated with bubble formation.

NOTE 3—Copper-3 solution is also identified as in MEMC etch in reference publications.

NOTE 4—Sopori and Sato etches have been suggested for use in Table 1 and may be added when solution information and pictures become available from sponsors.

8.2 *Sample Preparation*:

8.2.1 Most silicon samples have residual oxide on the surface, either thermally grown as part of the fabrication process or occurring naturally due to exposure to air.

8.2.2 Immediately before defect etching, submerge the sample in concentrated HF solution for 1 min or until the surface becomes hydrophobic to remove surface oxide layers.

8.2.3 Rinse and hold the samples in deionized water until transferred to the etching solution.

8.3 *Defect Etching*:

8.3.1 As stated in Section 5, no standard design for etching systems exists. This example describes a simple system:

8.3.1.1 Place the specimen in the bottom of a Hf-proof beaker with the surface to be inspected facing upward.

8.3.1.2 Pour in sufficient etchant to cover the specimen with about 2 cm of solution.

8.3.1.3 Maintain 1 L of solution for each 1 000 cm of sample surface area to control temperature effects.

8.3.1.4 Etch the specimen according to the removal and agitation restriction provided in the selection tables. The time of the etching process may be derived by use of the suggested etching depth for specific defects. Suggested removals may be found in the Practices F 1725, F 1727, and Guide F 1726.

8.3.1.5 If the etching solution must be contained at the point of use, decant the solution into a container for (hazardous) waste and rinse the specimen thoroughly with running water. If the solution is chromium-free and is not contained for disposal,

TABLE 1 Classification Of Application And Issue Suitability For Chromium-Free Solutions[A]

Chromium-Free Solutions			Applications											Issues			
Solution Name	Recipe	EST ~ etch rate ~ ~ in microns per min	100 ORIENTATION	111 ORIENTATION	P- TYPE	P+ TYPE	N- TYPE	N+ TYPE	OISF	SHALLOW PITS	HILLOCKS	DISLOCATIONS	EPI SF	BUBBLE FORMING	AGITATION REQ	TEMPERATURE	FLOW PATTERNS
Copper-3 [Figs. 17 and 18]	$HF:HNO_3:HAc:H_2O$: $Cu(NO_3)_2$• $3H_2O$ @ 36 : 25 : 18 : 21 :1g/ 100ml TOTAL VOL.	1 (1µm per min) with vigorous agitation)	A	A	A	D	A	D	A	A	C	A	A	YES	YES	~25 °C	N0
Copper-3 [Figs. 18-24]	$HF:HNO_3:HAc:H_2O$: $Cu(NO_3)_2$• $3H_2O$ @ 36 : 25 : 18 : 21 :1g/ 100ml TOTAL VOL.	5	A	A	A	D	A	D	A	A	C	A	A	YES	NO	~25 °C	NO
Modified Dash [Figs. 25-32]	$HF:HNO_3:HAc:H_2O$ @ 1:3:12 0.17 $AgNo_3$ 0.005 to 0.05 g/l	5 (1µm per min with vigorous agitation)	A	A	A	C	A	D	A	A	-	A	A	YES	YES	~25 °C	NO

[A]Code:
A = Excellent
B = Good
C = Acceptable
D = Unacceptable

TABLE 2 Classification of Application and Issue Suitability for Chromium-Bearing Solutions[A]

Chromim-bearing Solutions			Application											Issues			
Solution Name	Recipe	EST in ~ Etch rate ~ ~ microns per min	100 ORIENTATION	111 ORIENTATION	P– TYPE	P+ TYPE	N– TYPE	N+ TYPE	OISF	SHALLOW PITS	HILLOCKS	DISLOCATIONS	EPI SF	BUBBLE FORMING	AGITATION REQ	TEMPERATURE	FLOW PATTERNS
[Figs. 1-6] (See Note 2)	HF:$K_3Cr_3O_7$(1.5*M*) @ 2 : 1	1	A	B	A	D	A	C	A	B	C	A	A	YES	YES	<30 °C	YES
Wright [Figs. 7-16]	HF:HNO_3:CrO_3(5*M*): HA_C:H_2O: $Cu(NO_3)_2$• $3H_2O$@ 2: 1: 1: 2: 2g/240 mL total Volume	0.6	A	A	A	B	A	C	A	B	B	A	A	YES	YES	<30 °C	

[A]Code:
A = Excellent
B = Good
C = Acceptable
D = Unacceptable

the solution may be quenched with water and thoroughly rinsed in the same beaker.

8.3.1.6 Blow the specimen dry with filtered, organic free nitrogen.

8.3.1.7 Store the specimen in a clean container until inspected.

9. Keywords

9.1 defect density; dislocation; grain boundary; microscopic; polycrystalline imperfection; preferential etch; silicon; slip

APPENDIX

(Nonmandatory Information)

X1. SPONSORSHIP OF ADDITIONAL ETCHING SOLUTIONS

X1.1 This guide will be improved and expanded to included other etchants through the ASTM ballot process. The sponsor shall submit tabular information and pictures of etched defect examples (see Figs. 1-32) from Subcommittee F01.06 as follows:

X1.2 *Guidelines for Sponsors*:

X1.2.1 A preferential etching solution submitted as an addition to this guide must be sponsored by an individual willing to supply information for Table 2 or Table 1.

X1.2.2 Defect pictures, approximately 2.5 by 3 in.(60 mm by 75 mm) in size, demonstrating the applications of the solution shall include the following descriptive information:

(1) Image magnification (approximately 400x),

(2) Surface removal during etch (in microns),

(3) Relevant sample history (that is, thermal cycle type, resistivity, agitation, etc.), and

(4) OISF and dislocations for [100] and [111], also include applicable shallow pit (s-pits), hillocks, artifacts, and epitaxial defects.

X1.3 : Suggested additional information may be found in the following references:

REFERENCES

(**1**) Sirtl, E., and Adler, A. "Chromic Acid-Hydrofluoric Acid as Specific Reagents for the Development of Etching Pits in Silicon," *Zeitschrift fur Metalkunde,* Vol 52, 1961, p. 529.

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