SEMI MF1809-1110 (Reapproved 1115)
GUIDE FOR SELECTION AND USE OF ETCHING SOLUTIONS TO DELINEATE STRUCTURAL DEFECTS IN SILICON

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NOTICE: This Document was reapproved with minor editorial changes.

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1 Purpose

1.1 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.

1.2 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. This Guide provides information on the selection and application of appropriate etching solutions.

2 Scope

2.1 This Guide covers the formulation, selection, and use of chemical solutions developed to reveal structural defects in silicon wafers.

2.2 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 solutions and provides guidance for the user to select according to the need. Illustrations of results obtained with these etching solutions are provided in Figures 1 through 32.

2.3 This Guide is intended for use with other practices and test methods. SEMI MF1725 and SEMI MF1726 are practices for analysis of crystallographic perfection of silicon ingots and wafers, respectively, utilizing etching solutions found in this Guide, and followed by counting in accordance with the Test Method SEMI MF1810. SEMI MF1727 defines the procedures for oxidation of the wafer prior to etching, if that is required to expose the defect structures of interest. JIS H 0609 is a test method that covers the entire process of determining crystalline defects in silicon wafers.

2.4 Both this Guide and JIS H 0609 emphasize the use of etching solutions that do not contain chromic acid, which is biologically and ecologically very hazardous (see ¶ 7.6). Because of the hazardous nature of chrome containing etchants, the use of chromic acid containing etchants is prohibited in some jurisdictions located in various parts of the world.

NOTE 1: See Related Information 1 for a discussion of the relationships between this Guide and JIS H 0609.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 Complicating factors are different for each etchant. Research the choice of etchants in advance to ensure the method and solution are compatible with the sample and objectives. Commonly encountered problems are:

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

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

3.1.3 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.

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3.1.4 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.

3.1.5 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.

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

3.1.7 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.

4 Referenced Standards and Documents

4.1 *SEMI Standards and Safety Guidelines*

SEMI C18 — Specification for Acetic Acid

SEMI C28 — Specifications for Hydrofluoric Acid

SEMI C35 — Specifications and Guideline for Nitric Acid

SEMI M59 — Terminology for Silicon Technology

SEMI MF523 — Practice for Unaided Visual Inspection of Polished Silicon Wafer Surfaces

SEMI MF1725 — Practice for Analysis of Crystallographic Perfection of Silicon Ingots

SEMI MF1726 — Practice for Analysis of Crystallographic Perfection of Silicon Wafers

SEMI MF1727 — Practice for Detection of Oxidation Induced Defects in Polished Silicon Wafers

SEMI MF1810 — Test Method for Counting Preferentially Etched or Decorated Surface Defects in Silicon Wafers

4.2 *ASTM Standards*[1]

ASTM D5127 — Standard Guide for Ultra-Pure Water Used in the Electronics and Semiconductor Industries

4.3 *JIS Standards*[2]

JIS H 0609 — Test Methods of Crystalline Defects in Silicon by Preferential Etch Techniques

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 Acronyms, terms, and symbols related to silicon technology, including those used in this Guide, are listed and defined in SEMI M59.

6 Apparatus

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

6.1.1 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.

[1] ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, USA; Telephone: +1.610.832.9585, Fax: +1.610.832.9555, http://www.astm.org

[2] Japanese Standards Association, 4-1-24 Akasaka, Minato-ku, Tokyo 107-8440, Japan; Telephone: +81.3.3583.8005, Fax: +81.3.3586.2014, http://www.jsa.or.jp

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6.1.2 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.

7 Reagents and Materials

7.1 *Purity of Reagents* — Chemicals shall conform to the assay and impurity levels of Grade 1 SEMI Specifications where they exist. Reagents for which SEMI Specifications have not been developed shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[3] where such specifications are available. 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.

7.2 *Purity of Water* — Reference to water shall be understood to mean Type E-3 or better water as described in ASTM D5127.

7.3 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.

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

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

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

7.6 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.

7.7 Safety or protective gear should be worn while handling these acid solutions or their components. Safety requirements vary, but essential items 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 The following tables show two broad categories of solutions. The first group in Tables 1 and 3 includes only chromium-free etching solutions. Although uses may be limited, these solutions should be considered whenever appropriate. The second group in Tables 2 and 4 includes only solutions that contain chromium compounds. These do well for their intended applications, but they 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 (see ¶ 7.6). Exposure can cause cancer.

NOTE 2: Copper-3 solution is also identified as 'MEMC etch' in referenced publications.

[3] 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. Pharmacopeial Convention, Inc., (USPC), Rockville, MD.

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NOTE 3: Sopori and Sato etches have been suggested for inclusion in Tables 2 and 4, and these solutions may be added when solution information and pictures become available from sponsors (see Related Information 2 for the methodology by which new solutions can be added to the guide).

8.1.2 Tables 1 and 2 list the figure numbers of the etched defect examples for these etching solutions together with their etching rates.

8.1.3 Tables 3 and 4 classify the suitability of each listed etching solution for the various applications. In the tables,

- A = Excellent,
- B = Good,
- C = Acceptable, and
- D = Unacceptable.

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.

8.1.4 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 rank the various possible solutions and then select the most appropriate choice.

8.1.4.1 Although this Guide does not require a specific solution, it is highly recommended that chromium-free etching solutions should be used whenever possible, for environmental and biological reasons.

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 minute 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 No standard design for etching systems exists (see ¶ 6.1). In general, the procedures defined for the etching system available to the user of this Guide must be followed. A simple system for manual use is as follows:

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^2 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.

NOTE 4: Suggested removals may be found in SEMI MF1725 and SEMI MF1726.

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, 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 Related Documents

9.1 Additional information may be found in the following references that report details of various etching solutions:

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

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9.1.2 Secco d'Arragona, F. "Dislocation Etch for (100) Planes in Silicon." *J. Electrochem. Soc.,* **110** (1972): p. 948.

9.1.3 Schimmel, D.G. "Defect Etch for <100> Silicon Evaluation." *J. Electrochem. Soc.,* **126** (1979): p. 479.

9.1.4 Wright-Jenkins, M. "A New Preferential Etch For Defects in Silicon Crystals." *J. Electrochem. Soc.,* **124** (1977): p. 757.

9.1.5 Yang, K.H. "An Etch for the Delineation of Defects in Silicon." *J. Electrochem. Soc.,* **131** (1984): p. 1140.

9.1.6 Dash, W.C. "Copper Precipitation on Dislocations in Silicon," *J. Appl. Phys.,* **27** (1956): p. 1193.

9.1.7 Chandler, T.C. "MEMC Etch-A Chromium Trioxide-free Etchant for Delineating Dislocation and Slip in Silicon," *J. Electrochem. Soc.,* **137** (1990): p. 944.

9.1.8 Sopori, B.L. "A New Defect Etch for Polycrystalline Silicon," *J. Electrochem. Soc.,* **131** (1984): p. 667.

10 Keywords

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

Table 1 Recipes, Figure Index, and Approximate Etch Rates for Chromium Free Etching Solutions

Solution Name	*See Figures*	*Recipe*	*Approximate Etch Rate*
Copper-3	1–2 (with agitation)	$HF : HNO_3 : HAc : H_2O : Cu(NO_3)_2 \cdot 3H_2O$ @ 36 : 25 : 18 : 21 : 1 g/100 mL total volume	1 µm/min
Copper-3	3–8 (without agitation)	$HF : HNO_3 : HAc : H_2O : Cu(NO_3)_2 \cdot 3H_2O$ @ 36 : 25 : 18 : 21 : 1 g/100 mL total volume	5 µm/min
Modified Dash	9–16	$HF : HNO_3 : HAc : H_2O$ @ 1 : 3 : 12: 0.17 + $AgNO_3$ 0.005 to 0.05 g/L	1 µm/min

Table 2 Recipes, Figure Index, and Approximate Etch Rates for Chromium Containing Etching Solutions

Solution Name	*See Figures*	*Recipe*	*Approximate Etch Rate*
Secco	17–22	$HF : K_2Cr_2O_7$ (0.15 M) @ 2 : 1	1 µm/min
Wright	23–32	$HF : HNO_3 : CrO_3$(5 M) $: HAc : H_2O : Cu(NO_3)_2 \cdot 3H_2O$ @ 2 : 1 : 1 : 2 : 2 : 2 g/240 mL total volume	0.6 µm/min

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Table 3 Classification of Application and Issue Suitability for Chromium Free Etching Solutions[#1]

Solution Name	*Application*											*Issue*			
	100 Orientation	*111 Orientation*	*p-Type*	*P^+ Type*	*n-Type*	*n^+ Type*	*OISF*	*Shallow Pits*	*Hillocks*	*Dislocations*	*Epi Stacking Faults*	*Bubble Formation*	*Agitation Required*	*Temperature*	*Flow Patterns*
Copper-3 with Agitation	A	A	A	D	A	D	A	A	C	A	A	Yes	Yes	~25°C	No
Copper-3 without Agitation	A	A	A	D	A	D	A	A	C	A	A	Yes	No	~25°C	No
Modified Dash	A	A	A	C	A	D	A	A	-	A	A	Yes	Yes	~25°C	No

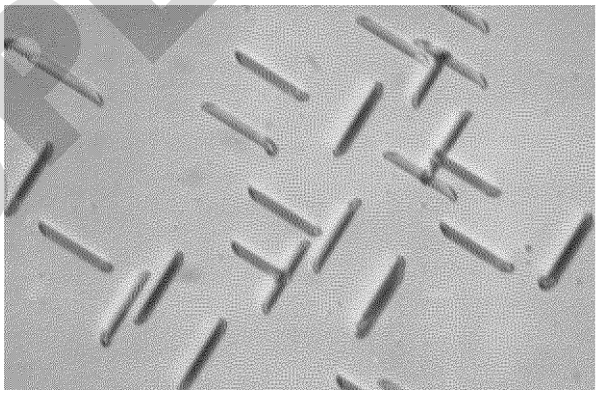
#1 Classifications in Tables 3 and 4 are as follows: A = Excellent, B= Good, C= Acceptable, D = Unacceptable.

Table 4 Classification of Application and Issue Suitability for Chromium Containing Etching Solutions[#1]

Solution Name	*Application*											*Issue*			
	100 Orientation	*111 Orientation*	*p-Type*	*P^+ Type*	*n-Type*	*n^+ Type*	*OISF*	*Shallow Pits*	*Hillocks*	*Dislocations*	*Epi Stacking Faults*	*Bubble Formation*	*Agitation Required*	*Temperature*	*Flow Patterns*
Secco[#2]	A	B	A	D	A	C	A	B	C	A	A	Yes	Yes	<30°C	No
Wright	A	A	A	B	A	C	A	B	B	A	A	Yes	Yes	<30°C	No

#1 Classifications are as follows: A = Excellent, B= Good, C= Acceptable, D = Unacceptable.

#2 Flow pattern defects form a characteristic '*v*' shaped pattern when the wafer is etched in a vertical position without acid agitation (see Figure 19). Other applications of Secco etch require some form of agitation to avoid confusing artifacts associated with bubble formation.



#1 type, 10 Ω·cm, (100) Wafer; 1100°C Steam, 80 minute Oxidation; Copper-3 Etch with Agitation; 2 µm removal.

Figure 1
Oxidation Stacking Fault, 500×

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