

SEMI C34-0699

SPECIFICATION AND GUIDELINE FOR MIXED ACID ETCHANTS

This specification and this guideline were technically approved by the Global Process Chemicals Committee and are the direct responsibility of the North American Process Chemicals Committee. Current edition approved by the North American Regional Standards Committee on April 23, 1999. Initially available on SEMI OnLine May 1999; to be published June 1999. This document replaces SEMI C2.1 and C7.19 in their entirety. Originally published in 1981 and 1995 respectively.

1 Purpose

1.1 The purpose of this document is to standardize requirements for mixed acid etchants used in the semiconductor industry and testing procedures to support those standards. Test methods have been shown to give statistically valid results. This document also provides guidelines for grades of mixed acid etchants for which a need has been identified. In the case of the guidelines, the test methods may not have been statistically validated yet.

2 Scope

2.1 The scope of this document is all grades of mixed acid etchants used in the semiconductor industry.

3 Limitations

3.1 None.

4 Referenced Documents

SEMI C1 — Specifications for Reagents

SEMI C2 — Specifications for Etchants

5 Terminology

mixed acid etchant — any combination of nitric, hydrofluoric, and acetic acids with the relative composition expressed in terms of volumes of 70% nitric acid, 49% hydrofluoric acid, and glacial acetic acid, respectively. In the expression, all the relative volumes shall be reduced to a ratio of the smallest whole numbers. For example, a 3:1:2 mixed acid etchant would imply a mixture of 3 volumes of 70% nitric acid, 1 volume of 49% hydrofluoric acid, and 2 volumes of glacial acetic acid. If a component is absent, its relative volume shall be taken as zero. For example, a 3:1:0 mixed acid etchant would imply that no acetic acid is present.

6 Composition

6.1 The content of each of the components of a mixed acid etchant shall be expressed on a weight/weight basis of the 100% acids in the total mixture. For the volume-to-weight conversion, the densities shall be taken as 1.415, 1.153 g/mL, and 1.050 g/mL for 70% nitric acid,

49% hydrofluoric acid, and glacial acetic acid, respectively.

7 Tolerances

Nitric Acid:	± 1.0% (± 0.16 meq/g)
Hydrofluoric Acid:	± 0.5% (± 0.25 meq/g)
Acetic Acid:	± 1.0% (± 0.17 meq/g)

8 Requirements

8.1 The requirements for mixed acid etchants for Grade 1 and Tier A are listed in Table 1.

9 Grade 1 Procedures

9.1 *Total Acidity* — Accurately weigh a sample containing 30 to 40 milliequivalents of acidity in a polyethylene weighing bottle. Transfer with water to a 250 mL polyethylene beaker and dilute to approximately 100 mL. Add 10 drops of phenolphthalein indicator solution and titrate with 1 N standardized sodium hydroxide to a faint pink end point. Calculate the total acidity (A):

$$\text{Total Acidity} \left(\frac{\text{meq}}{\text{g}} \right) = \frac{\text{mL} \times \text{N of NaOH}}{\text{Weight of sample (g)}} = A$$

9.2 *Hydrofluoric Acid* — Accurately weigh a sample containing 0.3 to 0.5 g of hydrofluoric acid in a polyethylene weighing bottle. Transfer with water to a polyethylene beaker and dilute to approximately 100 mL. Add 10 drops of phenolphthalein indicator solution and titrate with 1 N or stronger sodium hydroxide solution to a faint pink endpoint. Add 25 mL of Acetate Buffer for Hydrofluoric Acid Determination and 1 g of Eriochrome Cyanine R indicator mixture. Mix continuously by magnetic stirring and titrate with standardized aluminum chloride solution to a pink-purple endpoint.

$$\% \text{ Hydrofluoric Acid} = \frac{\text{mL} \times \text{HF factor of AlCl}_3 \text{ soln.}}{\text{Weight of sample (g)}}$$

9.3 *Nitric Acid* — Accurately weigh a sample containing 0.9 to 1.1 g of nitric acid in a polyethylene weighing bottle. Quantitatively transfer into a 100 mL volumetric flask containing 50 mL of 2% boric acid solution, dilute to volume with water, and mix thoroughly. Following the manufacturer's direction,

ready a spectrophotometer and set the wavelength to 302 nm. Transfer the sample solution to a 1 cm fused silica cell and measure the absorbance of the sample solution versus water. Read from a previously established calibration curve the grams of nitric acid present in the sample solution (see SEMI C2, Section 3.2, Determination of Nitric Acid by Ultraviolet Absorption Spectrophotometry).

$$\% \text{ Nitric Acid} = \frac{\text{grams of HNO}_3 \text{ calibration curve} \times 100}{\text{Weight of sample (g)}}$$

9.4 *Acetic Acid* — The acetic acid content is calculated by deducting the acidity found for each of the other components from the value for the total acidity.

$$\% \text{ Acetic Acid} = \left[A - \frac{\% \text{HF}}{2.001} - \frac{\% \text{HNO}_3}{6.302} \right] \times 6.005$$

9.5 *Arsenic and Antimony (as As)* — To 50 g of sample in a polyfluorocarbon dish, add 5 mL of hydrochloric acid and 5 mL of sulfuric acid. Mix gently and evaporate in a sandbath in a hood to dense fumes of sulfur trioxide. Cool, cautiously add 10 mL of water, and re-evaporate to dense fumes of sulfur trioxide. Cool, and cautiously wash into a generator flask with water to make a volume of 35 mL. Proceed as described in the General Method for Arsenic (and Antimony) under SEMI C1, Section 3.4.5, starting with the sentence which begins, "Swirl the flask..." Any red color in the silver diethyldithiocarbamate solution of the sample should not exceed that in the standard containing 0.0015 mg of arsenic (As).

9.6 *Trace Element Contents* — Determine the levels of specified trace elements and establish that they do not exceed the specification limits using a suitable emission spectrographic procedure (see SEMI C1, Section 3.5, for Guidelines for Determination of Trace Elements by Emission Spectrography).

10 Grade 2 Procedures

10.1 This section does not apply to this chemical.

11 Grade 3 Procedures

11.1 This section does not apply to this chemical.

12 Grade 4 Procedures

12.1 This section does not apply to this chemical.

13 Grade 5 Procedures

13.1 This section does not apply to this chemical.

14 VLSI Grade Procedures

14.1 This section does not apply to this chemical.

15 Tier A Procedures

15.1 Standardized test methods are being developed for all parameters at the purity levels indicated. Until standardized test methods are published, test methodology shall be determined by user and producer. The Process Chemicals Committee considers a test method to be valid only if there is a documented recovery study showing a recovery of 75 - 125%. Recovery is for a known sample spike at 50% of the specified level.

16 Tier B Procedures

16.1 This section does not apply to this chemical.

17 Tier C Procedures

17.1 This section does not apply to this chemical.

18 Tier D Procedures

18.1 This section does not apply to this chemical.

Table 1 Impurity Limits and Other Requirements for Mixed Acid Etchants

Previous SEMI Reference #	C2.1-95	C7.19-95
	Grade 1	Tier A
	(Specification)	(Guideline)
Aluminum (Al)	0.3 ppm max	10 ppb max
Antimony (Sb)	--	10 ppb max
Arsenic (As)	--	10 ppb max
Arsenic and Antimony (as As)	0.03 ppm max	--
Barium (Ba)	--	10 ppb max
Boron (B)	0.2 ppm max	10 ppb max