

SEMI C28-0301

SPECIFICATIONS AND GUIDELINES FOR HYDROFLUORIC ACID

These specifications and guidelines 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 October 17, 1999. Initially available at www.semi.org February 2001; to be published March 2001. This document replaces SEMI C1.8, C7.3, C8.3, and C11.3 in their entirety. Originally published in 1978, 1990, 1992, and 1994 respectively; previously published June 1999.

1 Purpose

1.1 The purpose of this document is to standardize requirements for hydrofluoric acid 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 hydrofluoric acid 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 hydrofluoric acid used in the semiconductor industry.

2.2 The VLSI grade purity level is typically required by semiconductor devices with geometries of 0.8–1.2 microns.

2.3 These standards do not purport to address safety issues, if any, associated with their use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

3 Limitations

3.1 None.

4 Referenced Documents

4.1 SEMI Documents

SEMI C1 — Specifications for Reagents

4.2 ASTM Standards¹

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

¹ American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: www.astm.org

4.3 DIN Documents²

DIN 50451, Part 1 — Determination of Trace Metals in Liquids (Silver, Gold, and Copper in Nitric Acid by AAS)

DIN 50451, Part 2 — Determination of Trace Metals in Liquids (Cobalt, Chromium, Copper, Iron, and Nickel in Hydrofluoric Acid with Plasma-Induced Emission Spectroscopy)

DIN 50451, Part 3 — Determination of Trace Metals in Liquids (Aluminum, Cobalt, Copper, Sodium, Nickel, and Zinc in Nitric Acid with ICP-MS)

NOTE 1: As listed or revised, all documents cited shall be the latest publications of adopted standards.

5 Terminology

5.1 None.

6 Physical Property (for information only)

Density at 25°C	1.15 g/mL
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7 Requirements

7.1 The requirements for hydrofluoric acid for Grades 1 and 2, VLSI Grade, and Tier B are listed in Table 1.

8 Grade 1 Procedures

NOTE 2: Each laboratory is responsible for verifying the validity of the method within its own operation.

8.1 Assay — Accurately weigh 1.4–1.5 mL of sample in polyethylene weighing bottle, sample, stopper immediately, and reweigh. To 50 mL of water in a plastic vessel, add the sample (loosen the stopper of the polyethylene bottle, and add both the container and the stopper with the sample). Add 0.1 mL of phenolphthalein indicator solution, and titrate with standardized 1 N sodium hydroxide to a slight, pink color.

$$\% \text{Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 2.001}{\text{Weight of sample (g)}}$$

² Deutsches Institut für Normung e.v.; available from Beuth Verlag GmbH, Burggrafenstrasse 4-10, D-1000 Berlin 30, Germany

8.2 Color — Dilute 2.0 mL of platinum-cobalt stock solution (APHA No. 500) to 100 mL with water. Compare this standard (APHA No. 10) with 100 mL of sample in HF resistant plastic tubes. View vertically over a white background. The sample must be no darker than the standard.

8.3 Fluosilicic Acid — Weigh 31 mL (36 g) of sample into a large platinum dish. Add 2 g of potassium chloride and 3 mL of hydrochloric acid and evaporate to dryness on a steam bath in a hood. Wash down the sides of the dish with a small amount of water, add 3 mL of hydrochloric acid, and repeat the evaporation. Dissolve the residue in about 100 mL of water, cool to 0°C, and add 0.10 mL of phenolphthalein indicator solution. Neutralize any free acid with 0.1 N sodium hydroxide solution, keeping the temperature of the solution near 0°C. Heat the solution to boiling and titrate with 0.1 N sodium hydroxide. (The 0.1 N sodium hydroxide solution must be stored in a plastic bottle.)

$$\% \text{H}_2\text{SiF}_6 = \frac{\text{mL} \times \text{N of NaOH} \times 3.600}{\text{Weight of sample (g)}}$$

8.4 Chloride — Add 1.7 mL (2.0 g) of sample to 45 mL of water. Filter, if necessary, through a chloride-free filter. Add 1 mL of nitric acid and 1 mL of silver nitrate reagent solution. Any turbidity produced should be no greater than that produced when 0.01 mg of chloride ion (Cl) is treated as the sample.

8.5 Nitrate — Weigh 3.3 g of sample in a white plastic 50 mL beaker and dilute with 4.5 mL of water. To another 50 mL plastic beaker, add 6.5 mL of water and 1 mL of standard nitrate solution containing 0.01 mg of nitrate (NO₃) per mL. To each solution, add 2.5 mL of brucine sulfate reagent solution and cautiously add with stirring 20 mL of sulfuric acid. Allow to stand for 10 minutes. The yellow color in the sample solution should be no greater than that in the standard solution.

8.6 Phosphate — Evaporate 9 mL (10 g) of sample to dryness in a platinum or other suitable dish on a steam bath in a hood. Dissolve the residue in 25 mL of 0.5 N sulfuric acid. Add 1 mL of ammonium molybdate reagent solution and 1 mL of p-(methylamino)phenol sulfate reagent solution. Allow to stand for 2 hours at room temperature. Any blue color should be no greater than that produced when 0.01 mg of phosphate ion (PO₄) is treated like the sample.

8.7 Sulfate and Sulfite (as SO₄) — To 18 mL (20 g) of sample in a platinum or other suitable evaporating dish, add about 10 mg of sodium carbonate and 1 mL of 30 hydrogen peroxide. Evaporate to dryness on a steam bath in a hood, wash down the sides of the dish with a small volume of water, and add 3 mL of perchloric acid. Evaporate to about 1 mL, dilute with about 15 mL

of water, and add 0.01 mL of phenolphthalein indicator solution. Neutralize with ammonium hydroxide, dilute with water to 20 mL, and add 2 mL of dilute hydrochloric acid (1 + 19) and 2 mL of barium chloride reagent solution. Any turbidity should not exceed that produced by 0.1 mg of sulfate ion (SO₄) in an equal volume of solution containing the quantities of reagents used in the test. Compare 10 minutes after adding the barium chloride to the sample and standard solutions.

8.8 Arsenic and Antimony (as As) — To 87 mL (100 g) of sample in a fluoroplastic beaker, add 20 mL of nitric acid, 5 mL of sulfuric acid, and 5 mL of hydrochloric acid; mix gently after each addition. Evaporate to dense fumes of sulfur trioxide in a sand bath in a hood. Cool, cautiously add 10 mL of water, and again 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 should not exceed that in the standard containing 0.003 mg of Arsenic (As).

8.9 Trace Metal Analysis — The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), boron (B), calcium (Ca), chromium (Cr), copper (Cu), gold (Au), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate recovery between 75–125% of a known sample spike for half of the value of each specified item.

8.9.1 Special Reagents

8.9.1.1 Nitric Acid, Ultra Pure — Use nitric acid specified for ultra low metal ion content.

8.9.1.2 2% Nitric Acid Solution — Dilute 20 mL of ultra pure nitric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

8.9.2 Sample Preparation

8.9.2.1 In a clean environment, place 250 g of sample in a PTFE evaporating dish. Slowly evaporate on a hot plate, avoiding loss of sample by effervescence or spattering until approximately 2 mL of liquid remains.

NOTE 3: Evaporation typically requires 2 1/2 to 4 hours. Cool. Add 1 mL of ultra pure, 70% nitric acid. While maintaining volume, carefully warm several minutes to dissolve any residue. Cool. Transfer quantitatively to a 50 mL volumetric flask using 2% nitric acid for rinsing and dilution to volume. Run a reagent blank.