

SEMI C20-0301

SPECIFICATION AND GUIDELINES FOR AMMONIUM FLUORIDE 40%

This specification and these 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 November 22, 2000. Initially available at www.semi.org December 2000; to be published March 2001. This document replaces SEMI C1.3, C7.18, and C11.2 in their entirety. Originally published in 1978, 1995, and 1994 respectively. Previously published June 1999.

1 Purpose

1.1 The purpose of this document is to standardize requirements for ammonium fluoride 40% 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 ammonium fluoride 40% 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 ammonium fluoride 40% 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 This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the users of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

3 Limitations

3.1 None.

4 Referenced Standards

SEMI C1 — Specifications for Reagents

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	1.11 g/mL
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7 Requirements

7.1 The requirements for ammonium fluoride 40% for Grade 1, VLSI Grade, and Tiers A and B are listed in Table 1.

8 Grade 1 Procedures

8.1 **Assay** — Accurately weigh 3 g of sample in a polyethylene weighing bottle. Transfer with water to a polyethylene beaker and dilute to 100 mL. Add 40 mL of neutralized formaldehyde solution and stir magnetically for 15 minutes or allow to stand for 1/2 hour. Titrate with standardized 1 N sodium hydroxide to a slight pink color.

$$\% \text{Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 3.704}{\text{Weight of sample (g)}}$$

NOTE 2: *Neutralized formaldehyde solution:* Dilute 20 mL of 37% formaldehyde solution with 20 mL of water, add 0.1 mL of phenolphthalein indicator solution, and titrate with 0.1 N sodium hydroxide to a slight pink color.

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 Nessler tubes. View vertically over a white background. The sample must be no darker than the standard.

8.3 **pH of a 1% solution** — Dilute 2.5 mL (2.8 g) of sample to 100 mL with carbon dioxide- and ammonia-free water. Using a pH meter determine the pH at 25°C 1 to 2 minutes after immersion of electrodes. The pH range 6.0–7.5 corresponds to 0.2% free hydrogen fluoride (HF) to 0.2% ammonium hydroxide (NH₄OH) in the original solution.

8.4 **Chloride** — Mix 2.2 mL (2.5 g) of sample with 20 mL of water containing 0.5 g of boric acid. Add 1 mL of nitric acid and 1 mL of silver nitrate reagent solution, and allow to stand for 5 minutes. 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** — To 2 mL of water in a white plastic beaker, add 0.9 mL (1 g) of sample, 1 mL of sulfuric acid, 0.05 mL of 0.01 N (0.002 M) potassium permanganate, mix, and decolorize with sodium

arsenite reagent solution. Dilute to 50 mL with brucine sulfate reagent solution and mix. Heat the solution in a preheated (boiling water) bath for 10 minutes. Cool rapidly in an ice bath to room temperature. The yellow color of the sample should be no greater than that produced when 0.01 mg of nitrate ion (NO_3) is treated as the sample.

8.6 Phosphate — To a 9 mL (10 g) sample in a platinum dish, add 1 mL of sodium carbonate reagent solution and 40 mL of nitric acid. Evaporate carefully, to prevent spattering, to near dryness. Cool, wash down the sides of the dish with 5 mL of nitric acid, and evaporate to dryness. Repeat the evaporation with nitric acid two more times to ensure complete removal of all the fluoride. To the cooled dish, add 25 mL of 0.5 N sulfuric acid to dissolve the residue, warming if necessary. Cool, transfer to a color comparison tube, and add 1 mL of ammonium molybdate reagent solution, 1 mL of p-(methylamino)phenol sulfate reagent solution, and allow to stand at room temperature for 2 hours. Any blue color should be no greater than that produced when 0.01 mg of phosphate ion (PO_4) is treated as the sample.

8.7 Sulfate — To 23 mL (25 g) of sample, add 10 mL of sodium carbonate reagent solution and heat gently until sample has been volatilized. To the residue add 5 mL of hydrochloric acid and evaporate to dryness in a hood. Dissolve the residue in 10 mL of water and 1 mL of dilute hydrochloric acid (1 + 19); filter if necessary. Add 1 mL of barium chloride reagent solution, mix, and allow to stand for 10 minutes. Any turbidity developed should be no greater than that produced when 0.05 mg of sulfate ion (SO_4) solution is treated as the sample.

8.8 Arsenic and Antimony (as As) — To 30 mL (33 g) in a fluoroplastic beaker, add 20 mL of nitric acid and 5 mL of hydrochloric acid, and evaporate to dryness in a sand bath in a hood. Completely volatilize the ammonium fluoride, but do not bake. Add 10 mL of water and 5 mL of sulfuric acid and evaporate to dense fumes of sulfur trioxide. 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 that begins, "Swirl the flask..." Any red color in the silver diethyldithiocarbamate solution of

the sample should be no greater than that of the standard containing 0.001 mg of arsenic (As).

8.9 Trace Element Contents — By a suitable emission spectrographic procedure, determine for each of the specified trace elements that its content is not greater than the stated specification limit (see SEMI C1, Section 3.5, Guidelines for Emission Spectrography).

9 Grade 2 Procedures

9.1 This section does not apply to this chemical.

10 Grade 3 Procedures

10.1 This section does not apply to this chemical.

11 Grade 4 Procedures

11.1 This section does not apply to this chemical.

12 Grade 5 Procedures

12.1 This section does not apply to this chemical.

13 VLSI Grade Procedures

13.1 Specific procedures for this grade do not exist. Refer to Section 8 for available procedures.

14 Tier A Procedures

14.1 Standardized test methods are being developed for all parameters at the purity levels indicated. 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.

15 Tier B Procedures

15.1 Standardized test methods are being developed for all parameters at the purity levels indicated. The Process Chemicals Committee considers a test method to be valid 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 C Procedures

16.1 This section does not apply to this chemical.

17 Tier D Procedures

17.1 This section does not apply to this chemical.