

SEMI C23-0301

SPECIFICATIONS FOR BUFFERED OXIDE ETCHANTS

These specifications 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 C2.2 and C7.23 in their entirety. Originally published in 1981 and 1997 respectively; previously published June 1999.

1 Purpose

1.1 The purpose of this document is to standardize requirements for buffered oxide 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 buffered oxide 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 buffered oxide etchants used in the semiconductor industry.

2.2 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 Standards

SEMI C1 — Specifications for Reagents

4.2 ASTM Standards¹

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

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

5 Terminology

5.1 *buffered oxide etchant* — any combination of ammonium fluoride and hydrofluoric acid in which the concentrations are expressed in terms of the equivalent

relative volumes of 40% ammonium fluoride solution and 49% hydrofluoric acid. In the expression, the relative volumes shall be reduced to a ratio of the smallest whole numbers which properly describes the composition. For example, a 7:1 buffered oxide etchant contains the equivalent of 7 volumes of 40.0% ammonium fluoride and 1 volume of 49% hydrofluoric acid.

NOTE 2: Density at temperature.

6 Composition

6.1 For analytical purposes, the absolute concentrations of ammonium fluoride and hydrofluoric acid corresponding to the above definition shall be calculated according to the following equations.

$$\text{Weight \% NH}_4\text{F} = \frac{(\text{volume} \times \text{density} \times \text{concentration}) \text{NH}_4\text{F}}{(\text{volume} \times \text{density}) \text{NH}_4\text{F} + (\text{volume} \times \text{density}) \text{HF}}$$

$$\text{Weight \% HF} = \frac{(\text{volume} \times \text{density} \times \text{concentration}) \text{HF}}{(\text{volume} \times \text{density}) \text{NH}_4\text{F} + (\text{volume} \times \text{density}) \text{HF}}$$

where volume and density are expressed in consistent units and concentration is in weight percent to three significant figures.

6.2 Sample calculation for 7:1 buffered oxide etchant using 40.0% ammonium fluoride, density 1.111 g/mL, and 49.0% hydrofluoric acid, density 1.153 g/mL. The absolute percentage concentration of each component follows:

$$\text{Weight \% NH}_4\text{F} = \frac{7 \times 1.111 \times 40.0}{7 \times 1.111 + 1 \times 1.153} = 34.8\%$$

$$\text{Weight \% HF} = \frac{1 \times 1.153 \times 49.0}{7 \times 1.111 + 1 \times 1.153} = 6.33\%$$

7 Tolerances

7.1 The tolerances allowed for the absolute percentage of each of the components of a buffered oxide etchant shall be:

Ammonium Fluoride:	± 0.5%
Hydrofluoric Acid:	± 0.15%

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

7.2 For the example above, the permissible range of concentration for ammonium fluoride shall be $34.8 \pm 0.5\%$ and for hydrofluoric acid $6.33 \pm 0.15\%$.

8 Requirements

8.1 The requirements for buffered oxide etchants for Grades 1 and 2 are listed in Table 1.

9 Grade 1 Procedures

9.1 *Hydrofluoric Acid* — Weigh accurately approximately 4.0 grams of sample, transfer to a polyethylene beaker, and dilute with water to about 100 mL. Titrate with standardized 1 N sodium hydroxide. The endpoint may be detected colorimetrically by adding 3 drops of methyl red indicator solution and titrating to a definite yellow (no orange) endpoint. As an alternate method, the endpoint may be detected potentiometrically using an HF resistant pH electrode previously standardized in pH 4 and pH 7 buffers. Titrate to pH 6.5 with continuous stirring. Save the solution for the determination of ammonium fluoride.

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

9.2 *Ammonium Fluoride* — Add 40 mL of neutralized formaldehyde solution (see Section 9.2.1) to the solution from the preceding test and stir magnetically for 30 minutes. Titrate with standardized 1 N sodium hydroxide. The endpoint may be detected colorimetrically using 10 drops of phenolphthalein indicator and titrating to a stable pink end point. As an alternative method, the endpoint may be detected potentiometrically using an HF resistant electrode previously standardized in pH 7 and 9 buffers. Titrate to pH 8.5 with continuous stirring.

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

9.2.1 *Neutralized Formaldehyde Solution* — Dilute 20 mL of 37% formaldehyde solution with 20 mL of water and neutralize with 0.1 N sodium hydroxide solution to the phenolphthalein endpoint.

9.3 *Arsenic and Antimony (as As)* — To 30 mL (33 g) of sample in a polyfluorocarbon dish, add 20 mL of nitric acid and 5 mL of hydrochloric acid and evaporate in a sand bath in a hood to dryness. 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 reevaporate 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 0.001 mg of arsenic ion (As).

9.4 *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, Guidelines for Determination of Trace Elements by Emission Spectrography).

10 Grade 2 Procedures

NOTE 1: Each laboratory is responsible for verifying the validity of the method within its own operation.

10.1 *Hydrofluoric Acid* — Weigh accurately approximately 4.0 grams of sample, transfer to a polyethylene beaker, and dilute with water to about 100 mL. Titrate with standardized 1 N sodium hydroxide. The endpoint may be detected colorimetrically by adding 3 drops of methyl red indicator solution and titrating to a definite yellow (no orange) endpoint. As an alternate method, the endpoint may be detected potentiometrically using an HF resistant pH electrode previously standardized in pH 4 and pH 7 buffers. Titrate to pH 6.5 with continuous stirring. Save the solution for the determination of ammonium fluoride.

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

10.2 *Ammonium Fluoride* — Add 40 mL of neutralized formaldehyde solution (see Section 10.2.1) to the solution from the preceding test and stir magnetically for 30 minutes. Titrate with standardized 1 N sodium hydroxide. The endpoint may be detected colorimetrically using 10 drops of phenolphthalein indicator and titrating to a stable pink endpoint. As an alternative method, the endpoint may be detected potentiometrically using an HF resistant electrode previously standardized in pH 7 and 9 buffers. Titrate to pH 8.5 with continuous stirring.

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

10.2.1 *Neutralized Formaldehyde Solution* — Dilute 20 mL of 37% formaldehyde solution with 20 mL of water and neutralize with 0.1 N sodium hydroxide solution to the phenolphthalein endpoint.

10.3 *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