

SEMI C37-0699

SPECIFICATION FOR PHOSPHORIC ETCHANTS

This specification was technically approved by the Global Process Chemicals Committee and is 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 C2.3 in its entirety. Originally published in 1981.

1 Purpose

1.1 The purpose of this document is to standardize requirements for phosphoric 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 phosphoric 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 phosphoric 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

5.1 *phosphoric etchant* — any combination of phosphoric, nitric, and acetic acids with the relative composition expressed in terms of 85% phosphoric acid, 70% nitric 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 16:1:2 phosphoric etchant would imply a mixture of 16 volumes of 85% phosphoric acid, 1 volume of 70% nitric acid, and 2 volumes of glacial acetic acid. If a component is absent, its relative volume shall be taken as zero. For example, a 16:1:0 phosphoric etchant implies that no acetic acid is present.

6 Composition

6.1 The content of each of the components of a phosphoric etchant shall be expressed on a weight/weight basis of the 100 percent acid in the total mixture. For the volume-to-weight conversion, the densities shall be taken as 1.695, 1.415, and 1.050 g/mL for 85% phosphoric acid, 70% nitric acid, and glacial acetic acid, respectively.

7 Tolerances

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

Phosphoric Acid:	$\pm 1.0\%$ (± 0.20 meq/g)
Nitric Acid:	$\pm 0.5\%$ (± 0.08 meq/g)
Acetic Acid:	$\pm 0.5\%$ (± 0.08 meq/g)

8 Requirements

8.1 The requirements for phosphoric etchants for Grade 1 are listed in Table 1.

9 Grade 1 Procedures

9.1 *Total Acidity* — Weigh accurately 2.5 to 3.0 g of sample in a tared weighing bottle. Transfer with water to a 25 mL beaker and dilute to approximately 100 mL. Add 10 drops of thymolphthalein indicator solution and titrate with standardized 1 N sodium hydroxide solution to the blue endpoint. 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 *Phosphoric Acid* — Weigh accurately 2.5 to 3.0 g of sample in a tared weighing bottle. Quantitatively transfer the sample with 40 to 60 mL of water into a platinum or polyfluorocarbon dish. Evaporate the solution on a steam bath in a hood (1 to 2 hours). Rinse down the inner sides of the dish with 10 to 15 mL of water and re-evaporate for 1 hour. Cool and dilute with 50 mL of water. Add 10 drops of thymolphthalein indicator solution and titrate with standardized 1 N sodium hydroxide solution to the blue endpoint.

$$\% \text{ Phosphoric Acid} = \frac{\text{mL} \times \text{N of NaOH} \times 4.900}{\text{Weight of sample (g)}}$$

9.3 *Nitric Acid* — Weigh accurately a sample containing 0.9 to 1.1 g of nitric acid in a tared 100 mL volumetric flask. Dilute to volume with water and mix thoroughly. Following the manufacturer's directions, 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 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.

$$\% \text{ Acetic Acid} = \left[A - \frac{\% \text{H}_3\text{PO}_4}{4.900} - \frac{\% \text{HNO}_3}{6.302} \right] \times 6.005$$

9.5 *Heavy Metals (as Pb)* — Dilute 6 g of sample to 30 mL with water. For the standard, add 0.02 mg of lead ion (Pb) to a 5 mL aliquot of this solution and dilute to 25 mL with water. For the sample, use the remaining 25 mL portion. Adjust the pH to between 3 and 4 (using a pH meter) with 1 N acetic acid or dilute ammonium hydroxide (10% NH₃), dilute to 40 mL with water, and mix. Add 10 mL of freshly prepared hydrogen sulfide water to each and mix. Any color in the solution of the sample should not exceed that in the standard.

9.6 *Antimony* — Dilute 20 mL (20 g) of stock solution to volume with water in a 100 mL volumetric flask and mix. For the standard, dilute 0.4 mg of antimony ion (Sb) to volume with water in a second 100 mL volumetric flask and mix. Following the manufacturer's directions, ready an atomic absorption spectrometer, use an air-acetylene flame, position the antimony hollow cathode lamp, and set the monochromator to the antimony resonance line of 217.6 nm. Employ deuterium lamp correction. Aspirate water and set to zero absorbance. Then aspirate, in succession, the standard, water, and sample. The absorbance of the sample should not exceed that of the standard. (see SEMI C1, Section 3.6, Guidelines for Determination of Trace Elements by Atomic Absorption Spectrometry.)

9.6.1 *Stock Solution for Sections 9.6 through 9.9* — To 200 g of sample in a 400 mL beaker, add 100 mL of water. Heat to boiling on a hot plate in a hood, and boil off approximately 100 mL. Cool slightly, add 100 mL of water, and again boil off about 100 mL. Cool, transfer to a 200 mL volumetric flask, and dilute to volume with water. One mL contains 1 gram of sample.

9.7 *Arsenic* — To 10 mL (10 g) of stock solution in a 125 mL arsine generator flask, add 30 mL of water 10 mL of ferric ammonium sulfate reagent solution, and then 2% potassium permanganate reagent solution dropwise to a permanent pink color. Add 1.5 g of sodium chloride and mix to dissolve. Heat nearly to boiling, remove from heat, and add 1 mL of stannous chloride reagent solution. Dilute to 60 mL and cool to 25°C ± 3°C. For the standard, add 20 mL of dilute sulfuric acid (1 + 4) to 0.005 mg of arsenic ion (As) in a

second arsine generator flask and treat as above. Assemble the arsenic test apparatus (see SEMI C1, Section 3.4.2). Pack each scrubber tube with two pledgets of lead acetate-impregnated glass wool previously moistened with lead acetate solution, freed from excess solution by squeezing, and dried in a vacuum. Allow a small space between the two pledgets. Place 3.0 mL of silver diethyldithiocarbamate solution in each absorber tube and 10 g of zinc (granular) in each generator flask. Immediately connect the scrubber absorber assemblies to the sample and standard generator flasks. Place the flasks in a water bath maintained at 25°C ± 3°C. Swirl each flask occasionally. After 30 minutes disconnect the tubing from the generator flasks and transfer the silver diethyldithiocarbamate solutions to separate 1 cm photometer cells. Measure both sample and standard absorbances at 540 nm using the silver diethyldithiocarbamate solution as a blank. The absorbance of the sample should not exceed that of the standard.

9.8 *Manganese* — Add 25 mL (25 g) of stock solution to 100 mL of dilute sulfuric acid (1 + 9). For the standard, add 5 mL (5 g) of stock solution and 0.01 mg of manganese ion (Mn) to 100 mL of dilute sulfuric acid (1 + 9). To each solution, add 20 mL of nitric acid, heat to boiling, and continue boiling gently for 5 minutes. Cool slightly, add 0.25 g of potassium periodate, and again boil for 5 minutes. Any pink color in the sample solution should not exceed that in the standard.

9.9 *Copper, Iron, and Nickel* — Dilute 1 mL (1 g) of stock solution with 50 mL of water in a 100 mL beaker. Add 0.5 mL of ammonium hydroxide and cool. For the three-element standard, add 0.002 mg of copper ion (Cu), 0.01 mg of iron ion (Fe), and 0.003 mg of nickel ion (Ni) to 50 mL of water in a second 100 mL beaker.

9.9.1 Treat each solution as follows: Adjust the pH to 2.5 (using a pH meter) with dilute ammonium hydroxide (10% NH₃) or 10% hydrochloric acid. Transfer to a polyfluorocarbon-stoppered 250 mL separatory funnel. Rinse the beaker with water adjusted to pH 2.5 and add the rinsings to the funnel (the final volume should not exceed 100 mL). Add 10 mL of freshly prepared 1% ammonium 1-pyrrolidinedicarbodithiolate solution and mix thoroughly. Add 10.0 mL of water-saturated methyl isobutyl ketone (that is, 4-methyl-2-pentanone), stopper, and shake vigorously for 3 minutes. Allow the layers to separate. Drain and discard the lower, aqueous layer; save the upper, organic layer.

9.9.2 Following the manufacturer's directions, ready the atomic absorption spectrometer for measurements in the absorbance mode and with the air-acetylene flame adjusted for aspiration of an organic solvent. For copper, align the copper hollow cathode lamp, set the wavelength to 324.7 nm, and zero the absorbance while