

# SEMI MF1982-1110

## TEST METHODS FOR ANALYZING ORGANIC CONTAMINANTS ON SILICON WAFER SURFACES BY THERMAL DESORPTION GAS CHROMATOGRAPHY

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### 1 Purpose

1.1 Organics are present in many materials, such as plastics, lubricants, cleansers, soaps, and living tissues. Some of these compounds are volatile and others can become airborne through chemical reactions, heating, abrasion, or outgassing. Also they can transfer to wafers by direct contact or be left behind from solvent residues. Once present in clean facilities, they can deposit on wafer surfaces. Organics deposited on wafers can cause degradation haze, wafer surface tension changes, irregular oxidation rates, and other effects, such as counter-doping by organophosphorus compounds. Identification of trace level organic contaminants is important in determining the source of the particular contamination. These test methods use the thermal desorption gas chromatography (TD-GC)<sup>1,2</sup> technique to characterize and quantify organics deposited on wafer surfaces.

1.2 Monitoring of organic contamination on wafer surfaces also can be used to measure material outgassing for proper selection of cleanroom, construction, and wafer packaging materials.

### 2 Scope

2.1 These test methods cover the identification and quantification of organic contaminants on silicon wafer surfaces using a gas chromatograph interfaced to a mass spectrometer (GC-MS) or a phosphorus selective detector, or both.

2.2 These test methods describe the apparatus and related procedures for sample preparation and analyses by TD-GC.

2.3 The range of detection limits of these test methods depends on the target organic compounds, for example, the range of detection limits is from the subpicogram to the nanogram level of hydrocarbons (C<sub>8</sub> to C<sub>28</sub>) per square centimeter of silicon wafer surface.

2.4 These test methods can be used for polished silicon wafers, or silicon wafers with oxide films.

2.5 Two methods are described. Method A is performed on cleaved wafers. Method B is performed on full wafers. The detailed procedures of Method A and Method B as well as the differences between them, are described in § 5 and § 7.

2.6 Suitable safety precautions must be followed when handling organic solvents and compounds, hot materials subjected to propane flame, the propane flame itself, wafer thermal desorption systems, rapid thermal annealer, or a high temperature furnace.

**NOTICE:** 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 or other limitations prior to use.

### 3 Referenced Standards and Documents

#### 3.1 SEMI Standard

SEMI M59 — Terminology for Silicon Technology

1 Ferguson, L.A., "Analysis of Organic Impurities on Silicon Wafer Surfaces." *Microcontamination*, April 1986: pp. 33–7.

2 Saga, K. and Hattori, T., "Identification and Removal of Trace Organic Contamination on Silicon Wafers Stored in Plastic Boxes," *Journal of Electrochemical Society* (1996): pp. 3270–84.

### 3.2 ASTM Standard

ASTM D6196 — Practice for Selection of Sorbents and Pumped Sampling/Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air<sup>3</sup>

**NOTICE:** Unless otherwise indicated, all documents cited shall be the latest published versions.

## 4 Terminology

4.1 General acronyms, terms, and symbols related to silicon technology are listed and defined in SEMI M59.

### 4.2 Abbreviations Specific to this Standard

4.2.1 *AED* — atomic emission detector

4.2.2 *C*<sub>16</sub> — n-hexadecane (n-C<sub>16</sub>H<sub>34</sub>)

4.2.3 *FID* — flame ionization detector

4.2.4 *FPD* — flame photometric detector

4.2.5 *GC* — gas chromatography

4.2.6 *GC-MS* — gas chromatograph interfaced to a mass spectrometer

4.2.7 *MS* — mass spectrometer

4.2.8 *NPD* — nitrogen/phosphorus thermionic ionization detector

4.2.9 *TBP* — tributyl phosphate (C<sub>4</sub>H<sub>9</sub>O)<sub>3</sub>PO

4.2.10 *TCEP* — tris (2-chloroethyl) phosphate (ClCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>PO

4.2.11 *TD* — thermal desorption

4.2.12 *TP* — total organophosphorus

### 4.3 Definitions of Term Specific to this Standard

4.3.1 *blank wafer* — a thermally-treated wafer desorbed of any surface organic contaminants

## 5 Summary of Test Methods

### 5.1 Method A

5.1.1 *Desorption and GC Analysis* — The volatile organic contaminants on a wafer surface are desorbed thermally from the wafer surface in a wafer desorption oven and swept into a sample thermal desorption tube. The sample thermal desorption tube then is heated for a set period in the thermal desorption unit and the volatile organic contaminants desorbed from the sample thermal desorption tube are swept by a stream of helium to a cold trap where they are preconcentrated. At the end of this period, the cold trap is heated rapidly to release the trapped organics to the GC column head. Sample components then are separated and eluted out of the GC column. Then, a portion goes to a phosphorus selective detector and the remainder goes to a mass spectrometer (MS). Blank wafers are prepared by purging out any surface organic contaminants in a rapid thermal annealer or a high temperature furnace while a purge gas is flowing.

5.1.2 *Identification of Contaminants* — Identification of individual unknown compounds is performed by correspondence of retention time of their peaks with that of known compounds. Correspondence of retention time on a single column should not be regarded as proof of identity. More precise identification of individual unknown compounds is performed with MS by matching their fragmentation patterns with mass spectra of known compounds in the spectral library.

5.1.3 *Quantification* — Quantification of total organics is based on the comparison of the integrated total peak area of the sample peaks with the area of the external standard compound, n-hexadecane (n-C<sub>16</sub>H<sub>34</sub>) [C<sub>16</sub>]. Total

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organophosphorus content in a sample is quantified by comparing the sample signal integrated from the phosphorus selective detector with the signal of the phosphorus standard compound, tris (2-chloroethyl) phosphate (TCEP) or tributyl phosphate (TBP). Specified range of standards is measured periodically, and the result is reported with blank wafer data.

## 5.2 Method B

**5.2.1 Desorption and GC Analysis** — The volatile organic contaminants on a wafer surface are desorbed thermally from the wafer surface in a quartz chamber unit and swept into a glass TD tube. The glass TD tube then is heated for a set period and a stream of helium sweeps the volatile organic contaminants desorbed from the glass TD tube to a cold trap where they are preconcentrated. At the end of this period, the cold trap is heated rapidly to release the trapped organics to the GC column head. Sample components then are separated and eluted out of the GC column. Then, a portion goes to a phosphorus selective detector and the remainder goes to a MS. Blank wafers are prepared by purging out any surface organic contaminants in the heated quartz chamber unit, while helium gas is flowing as a purge gas.

**5.2.2 Identification of Contaminants** — Identification of individual unknown compounds is performed by correspondence of retention time of their peaks with that of known compounds. Correspondence of retention time on a single column should not be regarded as a proof of identity. More precise identification of individual unknown compounds is performed with MS by matching their fragmentation patterns with mass spectra of known compounds in the spectral library.

**5.2.3 Quantification** — Quantification of total organics is based on the comparison of the integrated total peak area of the sample peaks with the area of the external standard compound,  $C_{16}$ . Total organophosphorus content in a sample is quantified by comparing the sample signal integrated from a phosphorus selective detector with the signal of the phosphorus standard compound, tris-(2-chloroethyl)-phosphate (TCEP) or tributyl phosphate (TBP). Specified range of standards is measured periodically, and the result is reported with blank wafer data.

## 6 Apparatus

### 6.1 Method A

**6.1.1 GC Instrument** utilizing a capillary column to separate a wide variety of organic compounds coupled to a MS, or a phosphorus selective detector, or both. Examples of phosphorus selective detectors are flame photometric detector (FPD), and atomic emission detector (AED). The nitrogen/phosphorus thermionic ionization detector (NPD) also responds to nitrogen containing compounds.

**NOTE 1:** A NPD may also be used as a phosphorus selective detector. This type of detector also responds to nitrogen containing compounds. If an NPD is used, the total organophosphorus reported should exclude any signals due to nitrogen containing compounds. Often, identification from the mass spectra can be used to determine whether compound contains nitrogen or phosphorus, or both.

**6.1.2 Sample Thermal Desorption Tubes** — Stainless-steel tubes packed with adsorbent medium, are used to trap compounds of interest and release them onto a thermal desorption unit.

**NOTE 2:** Note that stainless steel is catalytically active and can corrode with time, affecting recovery for some compounds. In this case, deactivated stainless steel, glass, or quartz tubes also can be used. Several adsorbent materials can be used for trapping organic compounds desorbed from silicon wafer samples. Some examples are activated carbon, graphitized carbon, and poly-(2,6-diphenyl-p-phenylene oxide).

**6.1.3 A thermal desorption unit** is used to desorb organics from sample thermal desorption tubes. The thermal desorption unit is coupled to the GC instrument via a heated transfer line, for example, heated to 225°C or above.

**6.1.4 A thermal annealer or a high temperature furnace** is used to obtain a blank wafer (see ¶ 7.1.1.2).

**6.1.5 A temperature controllable wafer desorption oven** is used to hold and heat a wafer desorption tube.

**6.1.6 Wafer Desorption Tube** — A stainless-steel tube with an approximate dimension: 12.7 mm (0.5 in.) in outer diameter, 9.53 mm (0.375 in.) in inner diameter and 254 mm (10 in.) in length (see Figure 1) is used to desorb organics from cleaved wafers. Larger tubes may be used for larger wafer sizes and to increase the sensitivity of the test (see Note 2).