



Designation: F 1982 – 99^{ε1}

Standard Test Methods for Analyzing Organic Contaminants on Silicon Wafer Surfaces by Thermal Desorption Gas Chromatography¹

This standard is issued under the fixed designation F 1982; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—The cold trap temperature in 7.2.3.1 was editorially corrected in October 1999.

1. Scope

1.1 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.

1.2 These test methods describe the apparatus and related procedures for sample preparation and analyses by thermal desorption gas chromatography (TD-GC)^{2,3}.

1.3 The range of detection limits of these test methods depend on the target organic compounds, for example, the range of detection limits will be subpicogram to nanogram level of hydrocarbons (C8 to C28)/ 1 cm² of a silicon wafer surface.

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

1.5 One of two methods can be performed. 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 difference between them, are described in Section 4 and 7.

1.6 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.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

D 6196 Practice for Selection of Sorbents and Pumped Sampling/Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air⁴

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *blank wafer*—in Method A, a thermally-treated wafer desorbed of any surface organic contaminants with a rapid thermal annealer or a high temperature furnace; in Method B—a thermally-treated wafer desorbed of any surface organic contaminants by purging them out in the heated quartz chamber unit while helium gas is flowing as a purge gas.

3.2 Abbreviations:Abbreviations:

3.2.1 AED—atomic emission detector.

3.2.2 C₁₆—n-hexadecane, n-C₁₆H₃₄.

3.2.3 FID—flame ionization detector.

3.2.4 FPD—flame photometric detector.

3.2.5 GC—gas chromatography.

3.2.6 MS—mass spectrometer.

3.2.7 NPD—nitrogen/phosphorus thermionic ionization detector.

3.2.8 TBP—tributyl phosphate, (C₄H₉O)₃PO.

3.2.9 TCEP—tris (2-chloroethyl) phosphate, (ClCH₂CH₂O)₃PO.

3.2.10 TD—thermal desorption.

4. Summary of Test Method

4.1 Method A:

4.1.1 *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

¹ These test methods are under the jurisdiction of ASTM Committee F01 on Electronics and is the direct responsibility of Subcommittee F01.06 on Silicon Materials and Process Control.

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² Ferguson, L.A., "Analysis of Organic Impurities on Silicon Wafer Surfaces," *Microcontamination*, Vol 4, No. 4, 1986, pp. 33-37.

³ Saga, K. and Hattori, T., "Identification and Removal of Trace Organic Contamination on Silicon Wafers Stored in Plastic Boxes," *Journal of Electrochemical Society*, Vol 143, Nov. 10, 1996, pp. 3270-3284.

⁴ *Annual Book of ASTM Standards*, Vol 11.03.

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.

4.1.2 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.

4.1.3 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, $n\text{-C}_{16}\text{H}_{34}$. Total 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.

4.2 Method B:

4.2.1 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 mass spectrometer (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.

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tributyl phosphate (TBP). Specified range of standards is measured periodically, and the result is reported with blank wafer data.

5. Significance and Use

5.1 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 TD-GC technique to characterize and quantify organics deposited on wafer surfaces.

5.2 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.

6. Apparatus

6.1 Method A:

6.1.1 GC Instrument, which utilizes a capillary column to separate a wide variety of organic compounds coupled to a mass spectrometer (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 nitrogen/phosphorus thermionic ionization detector (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 will need to 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 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 Thermal Desorption Unit, 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 Rapid Thermal Annealer, or a high temperature furnace used to obtain a blank wafer (see 7.1.1.2).

6.1.5 Temperature Controllable Wafer Desorption Oven, used to hold and heat a wafer desorption tube

6.1.6 *Wafer Desorption Tube*, 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 Fig. 1), used to desorb organics from cleaved wafers. Larger tubes may be used for larger wafer sizes and to increase the sensitivity of the test. As stated in 6.1.2, 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.

6.1.7 *Analytical Balance*.

6.1.8 *Quartz Plate and Carbide-Tipped Scribe*, used to cleave wafer samples.

6.1.9 *Quick Connect*, used to connect a nitrogen line to the wafer desorption tube.

6.2 *Method B:*

6.2.1 *GC Instrument*, which utilizes a capillary column to separate a wide variety of organic compounds, coupled to a mass spectrometer (MS) or a phosphorus selective detector, or both. Examples of phosphorus selective detectors are flame photometric detector (FPD), atomic emission detector (AED), or nitrogen/phosphorus thermionic ionization detector (NPD). The nitrogen/phosphorus thermionic ionization detector (NPD) also responds to nitrogen containing compounds (see Note 1).

6.2.2 *Quartz Chamber Unit*, used to desorb organic contaminants from the wafer surface and transfer them to a glass TD tube (see Fig. 2).

6.2.3 *Quartz Chamber*, may be used also to purge out any organic contaminants from a blank wafer.

6.2.4 *Glass TD Tube*, packed with adsorbent medium used to trap compounds of interest and release them onto a cold trap. 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).

6.2.5 *Cold Trap*, used to concentrate organics desorbed from glass TD tube and release the organics to a GC instrument by rapid heating.

7. Procedure

7.1 *Method A:*

7.1.1 *Sample Handling and Preparation:*

7.1.1.1 At all times, avoid manual handling of samples for analysis to prevent any secondary contamination of samples. Use stainless steel tweezers for sample preparation. Use a propane torch to flame stainless steel tweezers, weigh boats, and other accessories that come into direct contact with the sample before their usage.

7.1.1.2 Thermally desorb any organics from blank wafers in a rapid thermal annealer or a high temperature furnace. In

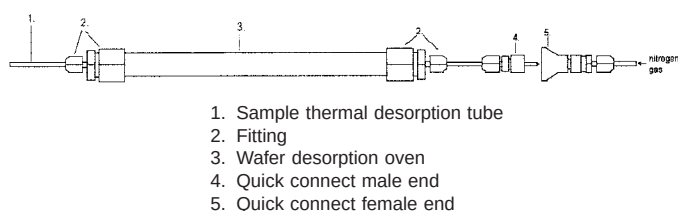


FIG. 1 Schematic of Wafer Desorption Setup

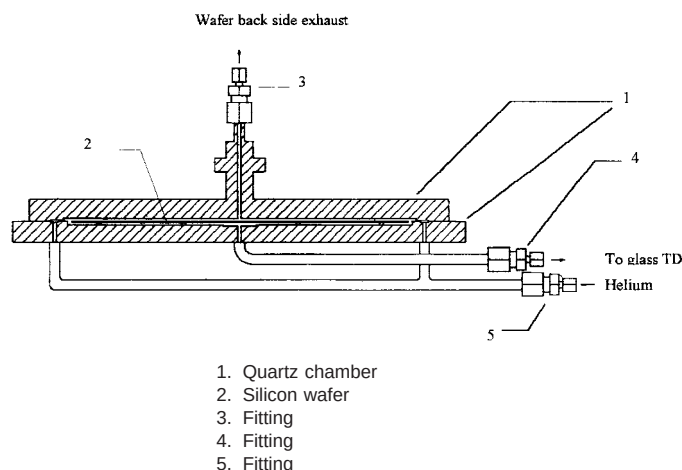


FIG. 2 Schematic of Quartz Chamber

order to desorb any organics from blank wafers, the temperature of a rapid thermal annealer is kept at 900 °C for 15 s, or the temperature of a high temperature furnace is kept at 700 °C for 30 min. Heating under air or oxygen will make a consistent organic-free SiO₂ surface. Place the thermally treated blank wafers directly into petri dishes and wrap the dishes with organic-free aluminum foil.

7.1.2 *Wafer Desorption:*

7.1.2.1 Clean and precondition sample thermal desorption tubes in accordance with Practice D 6196 prior to attaching to the wafer desorption tube.

7.1.2.2 Turn on the temperature controller for the wafer desorption oven and wait for the temperature to reach 275 °C.

7.1.2.3 Cleave the wafer sample into strips about 5 to 7 mm wide by scribing a line on the wafer where one wants it to break and then placing it on a straight wire and breaking it along the scribed line. The portion of the wafer sample needed for the analysis changes with the size of the wafer. For a 100-mm wafer, about half of its surface area is needed. Larger samples (having larger surface area) may be used to increase the sensitivity of the test.

7.1.2.4 Place the wafer strips of wafer into the wafer desorption tube. Attach a sample thermal desorption tube to the side of the wafer desorption tube. Connect the other end of the wafer desorption tube to a nitrogen line with a flow of 15 to 100 mL/min.

7.1.2.5 Place the wafer desorption tube in the oven and heat it for 30 min at 275 °C. This allows the volatile organics to be thermally desorbed from the sample wafer and transferred to the sample thermal desorption tube.

7.1.2.6 Seal both ends of the sample thermal desorption tube into the thermal desorption unit or by using caps if the thermal desorption-GC system is automated. Tubes must not be left open and exposed to the laboratory atmosphere. The end caps should be made of a material that has low outgassing and low reactivity properties, such as poly tetrafluoroethylene (PTFE), or stainless steel.

7.1.2.7 Analyze a blank wafer at least daily. Use a blank wafer treated with the same desorption procedure just described. Report blank data with the sample data.

7.1.3 *GC Analysis:*