SEMI C63-1108 (Reapproved 0618)
SPECIFICATION FOR ORGANOSILICATE PRECURSORS USED IN LOW K CVD PROCESSES

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1 Purpose

1.1 The purpose of this Document is to provide guidelines for organosilicate precursors used in Low K CVD processes and to standardize testing procedures to support those requirements. These test methods have been shown to give statistically valid results.

2 Scope

2.1 The scope of this Document lists the proposed impurity limits for organosilicate precursors (e.g., Dimethyldimethoxysilane, Octamethylcyclotetrasiloxane, Diethoxymethylsilane, Tetramethylcyclotetrasiloxane) used in the semiconductor industry.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 None.

4 Referenced Standards and Documents

4.1 *SEMI Standards and Safety Guidelines*

SEMI C1 — Guide for the Analysis of Liquid Chemicals

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

5 Terminology

5.1 None.

6 Physical Property (for information only)

	Dimethyldimethoxysilane	*Octamethylcyclotetrasiloxane*	*Diethoxymethylsilane*	*Tetramethylcyclotetrasiloxane*
Chemical Formula	$C_4H_{12}O_2Si$	$C_8H_{24}O_4Si_4$	$C_5H_{14}O_2Si$	$C_4H_{18}O_4Si_4$
CAS#	1112-39-6	556-67-2	2031-62-1	2370-88-9
Appearance	Clear Liquid	Clear Liquid	Clear Liquid	Clear Liquid
Density	0.88 gm/mL	0.956 gm/mL	0.83 gm/mL	0.991 gm/mL
Mol. Wt.	120.22 g/mol	296.62 g/mol	134.2 g/mol	240.51 g/mol
Boiling Point	82°C	175°C	95°C	134-135°C
Water Reactive	YES	NO	YES	NO

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7 Requirements

7.1 The requirements for organosilicate precursors for Grade 1 are listed in Table 1 (Water Reactive) and Table 2 (Water Non-Reactive).

8 Grade 1 Procedures

8.1 *Procedures for Water-Reactive Organosilicates*

8.1.1 *Assay/Alcohol* — The parameters cited have given satisfactory results. Alternative methods may be used as long as appropriate method validation as per SEMI C1 can be demonstrated.

8.1.1.1 Program a gas chromatograph fitted with a 60 m long × 320 µm ID × 5 µm 100% polydimethylsiloxane film column, a split injection port, and a thermal conductivity detector (TCD) according to the parameters in the Table.

Parameter	Setting
Oven	
Initial Temp [C]	50
Initial Time [min]	5
Ramp1 [C/min]	10
Temp1 [C]	250
Time1 [min]	10
Inlet	
Temperature [C]	190
Mode	Split
Split Ratio	15-1

Parameter	Setting
Detector (TCD)	
Temperature [C]	260
Reference Flow [mL/min]	20
Mode	Const Makeup
Makeup Flow [mL/min]	5
Column	
Flow	3.1 mL/min

8.1.1.2 Inject 5 µL of neat liquid sample and report the ratio of the major compound peak area to the total summed area of all components as the assay.

8.1.1.3 Report the ratio of primary alcohol peak area to the total summed area of all components.

8.1.2 *Chloride* — The parameters cited have given satisfactory results. Alternative methods may be used as long as appropriate method validation as per SEMI C1 can be demonstrated. Since chlorine can exist as volatile chlorosilanes, validation should use a chlorosilane spike.

8.1.2.1 The sample size and amount of water can be adjusted to account for higher or lower expected analyte concentrations. The ratio of water to organosilicate should be maintained at least at 1:1 or more to insure sufficient water is present to hydrolyze the organosilicate.

8.1.2.2 Add 5 mL of water to a 15 mL centrifuge tube. Add up to 5mL of organosilicate to the 15 mL centrifuge tube and record the weight of sample added.

8.1.2.3 Cap the tube and shake briefly. This will result in an exothermic reaction. Observe the contents of the tube. If the formation of bubbles is observed stop the sample preparation. Uncap the tube and allow bubbling to dissipate. The bubbling is probably due to the formation of hydrogen gas and must be removed before proceeding. If the pressure is not relieved, extremely high pressures can result.

8.1.2.4 Transfer the centrifuge tube to a mechanical shaker and shake for 30 minutes at 200 to 250 rpm. When shaking is completed, transfer the centrifuge tube to a water bath heated to 80°C to 85°C and heat for 1.5 to 2 hours with the cap secured. After heating, dilute the contents of the tube to 15 ml with deionized H_2O and record the volume.

8.1.2.5 Two layers should have formed at this point. Centrifuge the sample for 20 to 30 minutes to separate the upper aqueous layer from the lower organic layer. Analyze the aqueous portion by ion chromatography [SEMI C1] with conditions suitable to separate the chloride peak from any matrix peaks which may be present.

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8.1.3 *Boron* — The following method has been shown to recover volatile (e.g., triethylborate) forms of boron. Alternative methods may be used as long as appropriate method validation as per SEMI C1 can be demonstrated. Since boron can exist in organosilicates as volatile organoborates, it is important to perform the validation experiments with a volatile organoborate spike.

8.1.3.1 The sample size and amount of HF can be adjusted to account for higher or lower expected boron concentrations. The ratio of HF to organosilicate should be maintained at a 1.5:1 volume basis according to the following instructions since HF must be present in excess to fully remove the silicon matrix. The sample and HF volume listed below are satisfactory for boron concentrations of 1 ppb to 400 ppb.

8.1.3.2 Add 1 mL of 0.5% mannitol solution to a Teflon cup. Add 10 mL organosilicate sample the cup. Then swirl the mannitol and organosilicate in the cup a few seconds.

8.1.3.3 Add 15 mL of concentrated HF solution. **CAUTION:** Due to the strong exothermic reaction of water-reactive organosilicates and HF, the HF should initially be added in small aliquots (e.g., 1 mL) until addition no longer produces a strong reaction. The remaining HF can then be added in larger aliquots up to the total of 15 mL. Place the lid on the cup and place the cup into a water bath. Connect nitrogen inlet and outlet lines to each cup. Connect the outlet lines to a water-filled scrubber vessel to absorb HF and SiF_4 fumes that are evaporated from the sample.

8.1.3.4 Heat the water bath to 70°C and purge each vessel with 5 to 10 SCFH (standard cubic feet per hour) of nitrogen until less than 5 mL of solution remain. When <5 mL of HF mixture is left in each cup, add 5 mL of 0.2 M NH_4OH to the cup. Do not let the sample go to dryness at this step since boron will be evaporated as BF_3. If the sample goes to dryness, the sample must be re-prepared for analysis.

8.1.3.5 Evaporate the remaining solution to dryness. A small amount of solid (mannitol) will remain behind after evaporation. Do NOT let the sample remain at dryness for more than 1 hour as this can result in loss of boron and incorrect results. Dissolve the residue with 10 mL of 0.2 M NH_4OH solution. Allow at least 15 minutes for dissolution of the residue.

8.1.3.6 Analyze the sample using ICP-AES or ICP-MS using calibration standards prepared in 0.2 M NH_4OH solution.

8.1.4 *Metals* — The following method has given satisfactory results in determining trace metal impurities at the specified value for each of the following trace metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), iron, (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin, (Sn), titanium (Ti), vanadium (V), and zinc (Zn). Alternative methods may be used as long as appropriate method validation as per SEMI C1 can be demonstrated.

8.1.4.1 Fill a quartz or Teflon sample container with both an inlet-and outlet port with 50 to 100 g sample. Connect a filtered nitrogen purge and set the flow to 5 to 7 SCFH (standard cubic feet per hour). Heat the container to 60°C to 70°C using a suitable heat source.

8.1.4.2 Continue heating until each sample is completely evaporated. Remove the container from the heat source and allow the container to cool. Add 5 mL of 10% v/v HNO_3 acid to the container.

8.1.4.3 Place container back on heat source set to 90°C. Heat until condensation appears on the wall of the containers then for an additional 1.5 to 2 hours, stirring occasionally. Remove container from heat and allow cooling. Add 5 mL of water to each container. Transfer container contents to acid-soaked, water rinsed 15 mL centrifuge tube.

8.1.4.4 Analyze by ICP-MS [SEMI C1] using conditions suitable to reduce isobaric interferences. Calibrate the ICP-MS using matrix-matched 5% v/v HNO_3 acid calibration standards.

8.2 *Procedures for Water Non-Reactive Organosilicates*

8.2.1 *Assay* — The parameters cited have given satisfactory results. Alternative methods may be used as long as appropriate method validation as per SEMI C1 can be demonstrated.

8.2.1.1 *General Description* — A GC-FID using a non-polar polymethylsiloxane column is calibrated using standards of tetramethylcyclotetrasiloxane (TMCTS) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (7-MTSO) in hexane. Theoretical response factors for other impurities are calculated using relative response factors. Cyclic siloxane impurities use response factors based on TMCTS and linear siloxane impurities use response factors based on 7-MTSO. For OMCTS analysis, calibrate with octamethylcyclotetrasiloxane and 7-MTSO. After calibration, a neat liquid sample is injected into a gas chromatograph. The assay is calculated from the normalized area% of the main component relative to all impurities in the sample whose individual concentrations are calculated using the response factors (calibration factor).

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