Application Note

Instrument: O836Si

Determination of Oxygen in Silicon Wafers

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Introduction

In electronics, a wafer is a thin slice of semiconductor, typically crystalline silicon (c-Si), and is used for the fabrication of integrated circuits. The wafer serves as the substrate for microelectronic devices built in and upon the wafer. Currently, the most widely utilized method in the manufacturing of single crystal silicon involves melting silicon in a quartz crucible. As molten silicon is contained in a quartz crucible, it is contaminated with various impurities, the most abundant being oxygen, which originates from the interaction between Si and SiO_2 in the crucible. After cooling, silicon crystals can become supersaturated with oxygen. Thermal treatment cycles, which are typically employed in the fabrication of electronic devices, can cause the precipitation of this supersaturated oxygen in silicon wafers.* Oxygen precipitates located in the active device region of the wafer will impair the operation of the device and can result in shorter carrier lifetimes, increased leakage current, and reduced mechanical strength. Therefore, oxygen determination is a critical quality control parameter in the silicon wafer manufacturing process, as oxygen concentrations influence the electrical, thermal and mechanical properties of the silicon. Having the capability to monitor the oxygen content in silicon wafers provides manufacturers with the ability to modify and tailor their production methods to minimize oxygen concentrations in order to achieve the desired quality finished product.

**United States Patent No. 5,882,989: Process for the Preparation of Silicon Wafers Having a Controlled Distribution of Oxygen Precipitate Nucleation Centers, March 16, 1999*

Instrument Model and Configuration

The LECO O836Si was designed to meet the low-level sensitivity and high precision demands of the silicon industry. By combining the unmatched sensitivity of a solid-state infrared detection system with a novel sample loading system and a programmable impulse furnace, the O836Si provides accurate and precise oxygen results in materials such as silicon wafers.

The use of the Surface Oxide Removal functionality of the Cornerstone® brand software allows for separation of surface and bulk oxygen sources. Analysis results obtained following this procedure reflect bulk oxygen concentrations only. To quantify the surface and bulk oxygen concentration of silicon wafers, the *Cornerstone* software's Peak Find option will need to be utilized.

Sample Preparation

Proper preparation and handling* of solid silicon samples is critical. The recommended sample preparation procedure is outlined below:

1. Etch for two minutes in a Mixed Acid Etchant**
2. Rinse for two minutes in distilled water
3. Etch for two minutes in concentrated hydrofluoric acid
4. Rinse for two minutes in distilled water
5. Rinse for two minutes in isopropyl alcohol
6. Dry with warm air

**Samples should be handled using clean tweezers only.*
***Mixed Acid Etchant:*

- 57 volumes of 70% Nitric Acid
- 18 volumes of 49% Hydrofluoric Acid
- 25 volumes of Glacial Acetic Acid

Note: Extreme caution should be exercised when handling strong acids, and proper PPE should be utilized.

Sample Dimensions/Mass

Maximum Length:	0.475 in
Maximum Width:	0.275 in
Maximum Thickness:	0.095 in
Recommended Sample Mass:	0.30 to 0.40 g

Accessories

782-703† Large Outer Graphite Crucibles, 782-795HD† High Density Inner Graphite Crucibles, 611-351-182 Lower Electrode Tip, 766-053 Curved Crucible Tweezers, 760-138 Straight Sample Tweezers

†Note: The 782-703 Outer Graphite Crucibles can be reused many times (~20 replicates), but the 782-795HD Inner Graphite Crucibles can only be used once. When using a new outer crucible, it is recommended that the crucible be conditioned by performing three additional blank analysis cycles with the crucible prior to its use.

Reference Materials

LCRM®, LRM®, NIST, or other suitable reference materials. Due to the limited availability of silicon reference materials, steel reference materials can be used for calibration.

Note: Oxygen in silicon reference materials are very rare. Typically, steel reference materials are used for calibration. For steel reference materials, analysis is performed utilizing the Steel Calibration Furnace Method, with the Surface Oxide Removal step set to "off". For silicon reference materials and samples, analysis is performed utilizing the Silicon Wafer Furnace Method, with the Surface Oxide Removal step set to "on". Additionally, the 625-712-249 Loading Head Insert must be rotated when switching between analysis of steel reference materials and silicon wafers.

Carrier Gas Selection

Oxygen determination in silicon wafers can be performed utilizing either helium or argon as a carrier gas. Due to the significantly lower thermal conductivity of argon compared to helium, a reduced furnace power setting will be required when using argon as a carrier gas. This reduction in furnace power will subsequently slow the evolution of oxygen from the sample, requiring an extended integration time. This extended integration time will provide a full cycle analysis time of approximately seven minutes when using argon as a carrier gas, in comparison to a full cycle analysis time of approximately six minutes when using helium as a carrier gas.

Method Parameters

General Parameters	Helium Carrier Gas	Argon Carrier Gas
Sample Introduction	Automated Sample Drop	Automated Sample Drop
Analysis Delay	30 s	45 s
Auto Analyze on Mass Entry	No	No
Outgas Before Mass Entry	No	No
Wait for User to Load Sample	Yes	Yes
Vacuum On Time	7 s	7 s

Element Parameters	Helium Carrier Gas	Argon Carrier Gas
Element	Oxygen	Oxygen
Integration Delay	0 s	0 s
Starting Baseline	2 s	2 s
Use Comparator	No	No
Integration Time	70 s	85 s
Use Endline	Yes	Yes
Ending Baseline	2 s	2 s

Furnace Methods

Steel Calibration Furnace Method

Furnace Parameter	Helium Carrier Gas	Argon Carrier Gas
Furnace Control Mode	Power	Power

Outgas Parameter	Helium Carrier Gas	Argon Carrier Gas
Cycles	5	5
Power Mode	Constant	Constant
Power	5500†† W	5200†† W
Time	30 s	30 s
Cool Time	5 s	10 s

Surface Oxide Removal Parameter	Helium Carrier Gas	Argon Carrier Gas
Remove Surface Oxide	No	No

Temperature Sustain Settings	Helium Carrier Gas	Argon Carrier Gas
Temperature Sustain Mode	None	None

Analyze Furnace Settings, Step 1	Helium Carrier Gas	Argon Carrier Gas
Power Mode	Constant	Constant
Power	3800†† W	3000†† W

Furnace Methods continued on next page

Silicon Wafer Furnace Method

Furnace Parameter	**Helium Carrier Gas**	**Argon Carrier Gas**
Furnace Control Mode	Power	Power

Outgas Parameter	**Helium Carrier Gas**	**Argon Carrier Gas**
Cycles	5	5
Power Mode	Constant	Constant
Power	5500[††] W	5200[††] W
Time	30 s	30 s
Cool Time	5 s	10 s

Surface Oxide Removal Parameter	**Helium Carrier Gas**	**Argon Carrier Gas**
Remove Surface Oxide	Yes	Yes
Power Mode	Constant	Constant
Power	1600[††] W	1400[††] W
Time	50 s	60 s

Temperature Sustain Settings	**Helium Carrier Gas**	**Argon Carrier Gas**
Temperature Sustain Mode	None	None

Analyze Furnace Settings, Step 1	**Helium Carrier Gas**	**Argon Carrier Gas**
Power Mode	Constant	Constant
Power	3800[††] W	3000[††] W

[††]May vary based on line voltage. Level can be adjusted to improve recovery and/or reduce crucible burn-through.

Autocleaner Parameters

Parameter	
Autocleaner State	Enabled[‡]
Autocleaner Mode	During Analysis[‡]
Clean Time	8 s

[‡]When the Autocleaner Mode is set to "Disabled", the autocleaner state should be set to "Enabled, do not use in Analysis".

Procedure

NOTE: The following procedure outlines the steps that should be followed when using a steel reference material. If a silicon reference material is being used, then step 2 should be replaced by step 4, followed by step 3, and then step 5.

1. Prepare the instrument as outlined in the operator's instruction manual.
2. Determine the Reference Material blank.
   a. Log in a minimum of three Blank replicates, selecting Steel Calibration as the Furnace Method.
   b. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   c. Press the Analyze button on the instrument screen again. The loading head slide-block will close and the lower electrode will open.
   d. Clean the upper and lower electrode either manually or, if applicable, remove the crucibles and press the Analyze button again to clean with the automatic cleaner.
   e. Insert a 782-795HD Graphite Crucible into a previously conditioned 782-703 Graphite Crucible.
   f. Firmly place the graphite crucibles onto the lower electrode tip.
   g. Press the Analyze button on the instrument screen. The lower electrode will close and the analysis sequence will start and end automatically.
   h. Repeat steps 2b through 2g a minimum of three times.
   i. Set the blank following the procedure outlined in the operator's instruction manual.
3. Instrument calibration/drift correction.
   a. Log in a minimum of three Standard replicates.
   b. Weigh ~1.0 g of a steel reference material, or ~0.30 to 0.40 g of a silicon reference material.
   c. Enter the mass and sample identification into the appropriate replicate fields.
   d. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   e. Place the sample into the open port at the top of the loading head.
   f. Press the Analyze button on the instrument screen again. The loading head slide-block will close and the lower electrode will open.
   g. Clean the upper and lower electrode either manually or, if applicable, remove the crucibles and press the Analyze button again to clean with the automatic cleaner.
   h. Insert a 782-795HD Graphite Crucible Into a previously conditioned 782-703 Graphite Crucible.
   i. Firmly place the graphite crucibles onto the lower electrode tip.

j. Press the Analyze button on the instrument screen. The lower electrode will close and the analysis sequence will start and end automatically.
k. Repeat steps 3b through 3j a minimum of three times for each calibration/drift reference material used.
l. Calibrate/drift following the procedure outlined in the operator's instruction manual.
m. Verify the calibration by analyzing another suitable reference material following steps 3b through 3j and confirm that the results are within the acceptable tolerance range of that material.

4. Determine the Sample blank.
   a. Log in a minimum of three Blank replicates, selecting Silicon Wafers as the Furnace Method.
   b. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   c. Press the Analyze button on the instrument screen again. The loading head slide-block will close and the lower electrode will open.
   d. Clean the upper and lower electrode either manually or, if applicable, remove the crucibles and press the Analyze button again to clean with the automatic cleaner.
   e. Insert a 782-795HD Graphite Crucible Into a previously conditioned 782-703 Graphite Crucible.
   f. Firmly place the graphite crucibles onto the lower electrode tip.
   g. Press the Analyze button on the instrument screen. The lower electrode will close and the analysis sequence will start and end automatically.
   h. Repeat steps 4b through 4g a minimum of three times.
   i. Set the blank following the procedure outlined in the operator's instruction manual.
5. Analyze Samples.
   a. Log in the appropriate number of Sample replicates, selecting Silicon Wafers as the Furnace Method.
   b. Weigh ~0.30 to 0.40 g of a silicon sample.
   c. Enter the mass and sample identification into the appropriate replicate fields.
   d. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   e. Place the sample into the open port at the top of the loading head.
   f. Press the Analyze button on the instrument screen again. The loading head slide-block will close and the lower electrode will open.
   g. Clean the upper and lower electrode either manually or, if applicable, remove the crucibles and press the Analyze button again to clean with the automatic cleaner.
   h. Insert a 782-795HD Graphite Crucible into a previously conditioned 782-703 Graphite Crucible.
   i. Firmly place the graphite crucibles onto the lower electrode tip.
   j. Press the Analyze button on the instrument screen. The lower electrode will close and the analysis sequence will start and end automatically.
   k. Repeat steps 5b through 5j for each sample being analyzed.

Typical Results[#]

	Helium Carrier Gas			Argon Carrier Gas		
Sample	*Mass (g)*	*Oxygen (ppm)*	*Oxygen (ppma)*	*Mass (g)*	*Oxygen (ppm)*	*Oxygen (ppma)*
Silicon Wafer	0.3753	6.0	10.5	0.3672	5.9	10.4
Sample 1	0.3640	6.0	10.5	0.3898	5.9	10.4
	0.3715	6.0	10.5	0.3797	6.2	10.9
	0.3639	5.5	9.7	0.3664	5.8	10.2
	0.3693	6.0	10.5	0.3750	6.3	11.0
	Avg =	***5.9***	***10.2***	***Avg =***	***6.0***	***10.6***
	s =	***0.2***	***0.5***	***s =***	***0.2***	***0.4***
Silicon Wafer	0.3950	6.4	11.3	0.3944	6.6	11.6
Sample 2	0.3946	6.5	11.4	0.3909	6.2	10.8
	0.3931	6.0	10.6	0.3926	6.3	11.0
	0.3956	6.8	11.9	0.3929	6.6	11.5
	0.3926	6.0	10.6	0.3950	6.5	11.4
	Avg =	***6.4***	***11.1***	***Avg =***	***6.4***	***11.4***
	s =	***0.3***	***0.5***	***s =***	***0.2***	***0.5***

[#]*Results are based upon a linear, forced through origin calibration utilizing 502-935 (Lot: 0719) Steel LCRM @ 0.0028% O.*

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