

SEMI P32-1104

TEST METHOD FOR DETERMINATION OF TRACE METALS IN PHOTORESIST

This test method was technically approved by the Global Micropatterning Committee and is the direct responsibility of the Japanese Micropatterning Committee. Current edition approved by the Japanese Regional Standards Committee on July 23, 2004. Initially available at www.semi.org August 2004; to be published November 2004. Originally published September 1998.

NOTICE: This Standard or Safety Guideline has an Inactive Status because the conditions to maintain Current Status have not been met. Inactive Standards or Safety Guidelines are available from SEMI and continue to be valid for use.

1 Purpose

1.1 This document describes an outline of a quantitative analysis method on trace metal concentration. This standard is intended to promote communication between users and suppliers.

2 Scope

2.1 This document applies to a measurement of trace metal concentration in ppb level in photoresist by instrumental techniques, such as atomic absorption spectrometry, plasma ion source mass spectrometry, and inductively coupled plasma atomic emission spectrometry.

2.2 Object metals in this measurement are Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, K, and Na.

2.3 Either additional metals or fewer can be agreed upon between users and suppliers and are added to the measurement list.

2.4 The following method has given satisfactory results in determining trace metal impurities at the specified value for each of the target trace metals. Alternative methods or conditions may be used as long as appropriate studies demonstrate recovery between 75%–125% of a known sample spike for half the specification value. The results should be reported as within specification (below a certain value) or not in specification only (SEMI C1).

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3 Referenced Standards and Documents

3.1 SEMI Standards and Safety Guidelines

SEMI C1 — Guide for the Analysis of Liquid Chemicals

3.2 ASTM Standard¹

ASTM D1193 — Standard Specification for Reagent Water

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

4 Summary of Method

4.1 Photoresist test solution is prepared by dry ashing method or direct method. Then trace metals in the test solution are measured by atomic absorption spectrometry, plasma ion source mass spectrometry, or inductively coupled plasma atomic emission spectrometry. The trace metal concentration is determined using a working curve, which is obtained by measuring a standard solution.

¹ ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, USA; Telephone: 610.832.9585, Fax: 610.832.9555, <http://www.astm.org>

5 Terminology

5.1 Definitions

5.1.1 *blank test* — a measurement without the object photoresist, which is performed under the standard procedures.

5.1.2 *dilution factor* — numerical number that indicates final amount of solution divided by the initial amount of solution in the preparation of the photoresist process.

5.1.3 *direct method* — a sample preparation method for preparing samples for direct trace metal in photoresist. The materials are diluted with a solvent and then analyzed by the appropriate analytical instrument.

5.1.4 *dry ashing method* — a sample preparation method for preparing samples used in measuring trace metals in the photoresist. The photoresist is evaporated and decomposed to ash by heating. The ash is dissolved in a volumetric flask with acid and aqueous reagent, and then analyzed by the appropriate analytical instrument.

5.1.5 *plasma ion source mass spectrometry* — a method that isolates and measures quantitative metal element by mass spectrometer using plasma as excitation source. Inductively coupled plasma mass spectrometry (ICP-MS) and microwave induced plasma mass spectrometry (MIP-MS) belong to this category.

5.1.6 *working curve* — the relationship between known metal concentrations prepared by standard solutions and the observed values of instrumental analysis.

6 Apparatus

6.1 Measurement Equipment

6.1.1 Flame atomic absorption spectrometer (F-AAS) and ICP-MS can be applied to the dry ashing method.

6.1.2 Graphite furnace atomic absorption spectrometer (GF-AAS), electrothermal atomization atomic absorption spectrometer (ETA-AAS), ICP-MS, MIP-MS, and inductively coupled plasma atomic emission spectrometer (ICP-AES) can be applied to the direct method.

6.1.3 *Instrument Condition* — Recommended instrumental conditions are summarized in Table 1 for each target metal.

Table 1 Measurement Equipment and Metal Elements

Element	Atomic Absorption Spectroscopy	Plasma Ion Source Mass Spectrometry		ICP-Atomic Emission Spectrometer
		ICP-MS ^{#1}	MIP-MS ^{#2}	
Al	309.2 nm	²⁷ Al	²⁷ Al	396.2 nm
Ca	422.7 nm	⁴⁰ Ca, ⁴⁴ Ca ^{#3}	⁴⁰ Ca	393.4 nm
Cr	357.9 nm 359.4 nm	⁵² Cr, ⁵³ Cr ^{#3}	⁵² Cr	267.7 nm 283.6 nm
Cu	324.7 nm	⁶³ Cu, ⁶⁵ Cu	⁶³ Cu, ⁶⁵ Cu	324.8 nm
Fe	248.3 nm	⁵⁶ Fe, ⁵⁴ Fe ^{#3}	⁵⁶ Fe, ⁵⁴ Fe	259.9 nm
Mg	285.2 nm	²⁴ Mg, ²⁵ Mg, ²⁶ Mg	²⁴ Mg, ²⁵ Mg, ²⁶ Mg	279.6 nm
Mn	279.5 nm	⁵⁵ Mn ^{#3}	⁵⁵ Mn	257.6 nm
Ni	232.0 nm 341.4 nm	⁵⁸ Ni, ⁶⁰ Ni ^{#3}	⁵⁸ Ni, ⁶⁰ Ni	221.6 nm 231.6 nm
K	766.5 nm	³⁹ K, ⁴¹ K ^{#3}	³⁹ K, ⁴¹ K	766.5 nm
Na	589.0 nm	²³ Na	²³ Na	589.0 nm

#1 ICP-MS — Ar is used as the plasma generation gas.

#2 MIP-MS — N₂ is used as the plasma generation gas.

#3 Beware of interfering ion (see Table 2).

Table 2 Interfering Ions

<i>Object Metal</i>	<i>Interfering Ion</i>
^{39}K	$^{38}\text{Ar}^1\text{H}$
^{41}K	$^{40}\text{Ar}^1\text{H}$
^{40}Ca	^{40}Ar
^{52}Cr	$^{40}\text{Ar}^{12}\text{C}$, $^{36}\text{Ar}^{16}\text{O}$, $^{38}\text{Ar}^{14}\text{N}$
^{55}Mn	$^{40}\text{Ar}^{14}\text{C}^1\text{H}$, $^{40}\text{Ar}^{15}\text{N}$, $^{38}\text{Ar}^{16}\text{O}^1\text{H}$
^{56}Fe	$^{40}\text{Ar}^{16}\text{O}$, $^{38}\text{Ar}^{18}\text{O}$
^{58}Ni	$^{40}\text{Ar}^{18}\text{O}$

7 Vessels, Reagents, and Environment

7.1 Vessel

- 7.1.1 Quartz glass volumetric flask
- 7.1.2 Quartz glass measuring pipette
- 7.1.3 Quartz glass beaker
- 7.1.4 PTFE vessel
- 7.1.5 Platinum crucible

7.2 Reagents

- 7.2.1 *DI Water* — Resistivity $\geq 18.0 \text{ M}\Omega \cdot \text{cm}$ at 25°C per ASTM D1193.
- 7.2.2 *Organic Reagent* — Use commercially guaranteed reagent for trace metal analysis.
- 7.2.3 *Inorganic Reagent* — Use commercially guaranteed reagent for trace metal analysis.
- 7.2.4 *Standard Reagent* — Use the commercially guaranteed reagents which have certified trace metals concentration.

7.3 Environment

- 7.3.1 The measurement is recommended to be performed in a clean room or clean zone at constant temperature. The stability of temperature should be better than $\pm 2^\circ\text{C}$. Dry ashing method should be performed in a draft chamber with HEPA filter, if possible.
- 7.3.2 In the case of volumetric analysis, the measurement environment is set to the standard temperature of measuring tools such as volumetric flask and measuring pipette.

8 Procedures

- 8.1 *Flow Chart of Measurement* — Refer to Figure 1 as suggested analysis process.