

SEMI M85-0120

GUIDE FOR THE MEASUREMENT OF TRACE METAL CONTAMINATION ON SILICON WAFER SURFACE BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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1 Purpose

1.1 Reduction of surface metal contamination below a concentration in accordance with the ITRS road map is a key issue for silicon wafer quality for most of the leading-edge technology applications. This Document provides a guide for a high-sensitivity measurement of trace metal contamination on the surface of a semiconductor grade silicon wafer by using inductively coupled plasma mass spectrometry (ICP-MS).

1.2 This Guide describes the procedure for trace metal measurement, including the metal impurity collection method from a silicon wafer surface, scanning solution composition, and its optimization. In particular, the procedure of the collection method is described in detail because it influences the reliability of measurement data and reproducibility of each facility.

2 Scope

2.1 This Guide describes methods for the measurement of trace metal contamination on a silicon wafer surface. The decomposition of silicon oxide on silicon wafer, the collection of trace metal contamination from a wafer surface using mixture acid, measurements, and reports are described in this Guide.

2.2 This Guide covers an evaluated substrate wafer as a mirror-polished surface, annealed wafer, epitaxial growth wafer, diffusion wafer, and bonding wafer, which are nonpatterned surfaces. However, this Document also addresses the back side of a patterned wafer. Additionally, this Guide covers wafers that form native oxides and thermal oxides.

2.3 In the case of decomposition of silicon oxide on the silicon wafer and contamination collection from the wafer surface, a procedure with the recommended technique for the vapor phase decomposition (VPD) and the direct acid droplet decomposition (DADD) methods is presented (see ¶ 9.1).

2.4 In this Document, a scanning solution for collecting metal contamination from wafer surfaces is recommended for using the solution compositions optimized by ensuring recovery rate with 75% to 125% (see ¶¶ 5.2.3 and 9.1.1.1). Here, the scanning solution consists of hydrofluoric acid and hydrogen peroxide or nitric acid.

2.5 This Guide uses only ICP-MS (see ¶ 7.1) for the measurement of contamination on the wafer surface. The target elements of this method are sodium, magnesium, aluminum, potassium, calcium, chromium, manganese, iron, cobalt, nickel, copper, and zinc.

NOTE 1: In this analysis procedure, a mini environment such as a shipping box is used for temporary storage and transfer of a silicon wafer. To evaluate the trace metal contamination from a mini environment, SEMI E45 should be used.

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 *Interference of Polyatomic Ions* — Polyatomic ions of atmospheric components, acid in the sample solution and argon—since argon gas is used for forming inductively coupled plasma—are produced in the plasma. In addition, polyatomic ions of silicon are produced when the sample solution contains a silicon matrix. These polyatomic ions interfere with the measurement of the target element, for example, $^{40}\text{Ar}^{16}\text{O}$ on ^{56}Fe , ^{38}ArH on ^{39}K , and $^{29}\text{Si}^{19}\text{F}$ on ^{48}Ti . Therefore, the interference of polyatomic ions should be suppressed by the cool plasma method, the collision/reaction cell or a double focusing sector field ICP-MS (high resolution ICP-MS).

3.2 *Matrix Effects* — The scanning solution collected from the silicon wafer contains the silicon matrix. The sensitivity of ICP-MS decreases when the sample solution contains too high-concentration silicon matrix. In that case, the internal standard method, the standard addition method or the removal of the silicon matrix should be utilized; measurements without the matrix effects would then be possible.

3.3 In the case of the removal of the silicon matrix, considerable attention should be paid to loss by volatilization, production of precipitates, and contaminations from the environment.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI C1 — Guide for Analysis of Liquid Chemicals

SEMI E45 — Test Method for the Determination of Inorganic Contamination from Minienvironments using Vapor Phase Decomposition-Total Reflection X-ray Spectroscopy (VPD/TXRF), VPD-Atomic Absorption Spectroscopy (VPD/AAS), or VPD/Inductively Coupled Plasma-Mass Spectrometry (VPD/ICP-MS)

4.2 ISO Standards¹

ISO 8655-2 — Piston-Operated Volumetric Apparatus – Part 2: Piston Pipettes

ISO 8655-6 — Piston-Operated Volumetric Apparatus – Part 6: Gravimetric Methods for the Determination of Measurement Error

ISO 14644-1:1999 — Clean Rooms and Associated Controlled Environments – Part 1: Classification of Air Cleanliness

ISO 17331:2004 — Surface Chemical Analysis – Chemical Methods for the Collection of Elements from the Surface of Silicon-Wafer Working Reference Materials and Their Determination by Total-Reflection X-Ray Fluorescence (TXRF) Spectroscopy

4.3 JIS Standard²

JIS K 0133 — General Rules for Frequency Plasma Mass Spectrometry

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

5 Terminology

5.1 Abbreviations and Acronyms

5.1.1 *ICP-MS* — inductively coupled plasma mass spectrometry

5.1.2 *VPD* — vapor phase decomposition

5.1.3 *DADD* — direct acid droplet decomposition

5.2 Definitions

5.2.1 *collision/reaction cell* — the collision/reaction cell is a system to reduce the interference that polyatomic ions cause. Interference of polyatomic ions is reduced by the interaction between ions and gas (hydrogen, helium, ammonia, etc.) introduced into a cell.

5.2.2 *cool plasma* — the method to reduce interference of polyatomic ions of mainly argon origin by plasma generated with the low high-frequency power or high carrier gas flow quantity.

5.2.3 *recovery rate* — the recovery rate is the ratio (B/A) of the quantity (B) of the measured element to the quantity (A) of the element that is included in a sample, that is, the quantity (A) of the added element. The recovery rate is expressed as a percentage.

¹ International Organization for Standardization, ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland; Telephone: +41.22.749.01.11, <http://www.iso.org>

² Japanese Standards Association, 4-1-24 Akasaka, Minato-ku, Tokyo 107-8440, Japan; Telephone: +81.3.3583.8005, Fax: +81.3.3586.2014, <http://www.jsa.or.jp>

5.2.4 *scanning solution* — scanning solution implies a solution for the collection of trace metals from a wafer surface after the decomposition of silicon oxide by the VPD method. On the other hand, it also implies the solution for the decomposition of silicon oxide and the collection of trace metals from a wafer surface by the DADD method.

5.2.5 *vapor phase decomposition (VPD) box* — the VPD box is an airtight container composed of acid-resisting materials (e.g., polytetrafluoroethylene and polyfluoroalkoxyethylene) and equipped with wafer stands.

6 Summary

6.1 In this Guide, sample preparation methods such as the collection of trace metal contamination from wafer surface and measurement methods for the collected contamination are described. A simple flowchart of this Guide is shown in Figure 1.

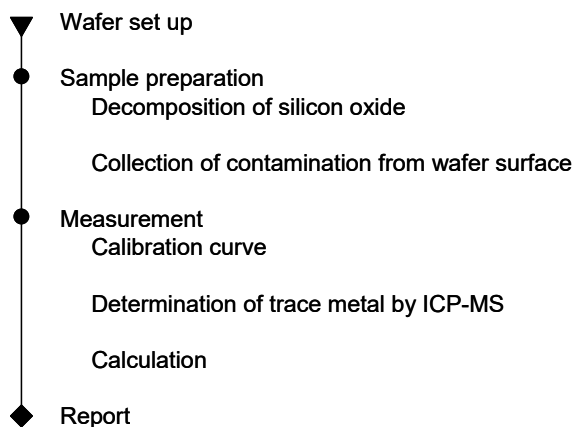


Figure 1
Flowchart of Contamination Analysis Procedure of Silicon Wafer Surface

6.2 *Sample Preparation* — This Guide specifies two methods for the collection of contamination; the VPD method and the DADD method. In the VPD method, silicon oxide is decomposed by hydrofluoric acid vapor and the contamination is collected from the wafer surface using the scanning solution droplet. On the other hand, in the DADD method, silicon oxide is decomposed using the scanning solution droplet, and the contamination is collected from the wafer surface using the droplet.

6.3 *Measurement* — After the sample preparation, the trace metal contamination in the sample solution is determined by ICP-MS.

7 Apparatus

7.1 There are two types of the instruments of ICP-MS. One is a quadrupole ICP-MS and the other is a high resolution ICP-MS. Either type of ICP-MS can be used for this Guide.

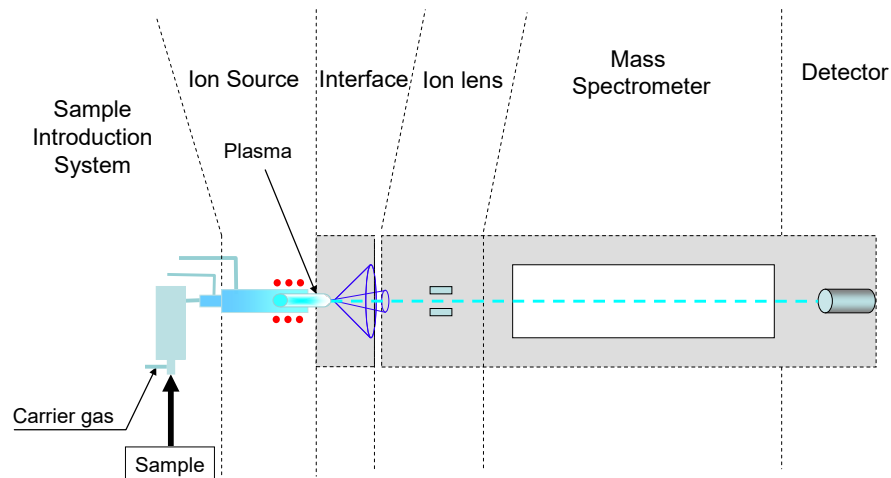


Figure 2
Schematic Diagram of ICP-MS Instrument
Typical System of ICP-MS

7.2 ICP-MS consists of a sample introduction system, an ion source, a sampling interface, ion lens, a mass spectrometer and a detector.

7.3 *Clean Booth* — The environment in a clean booth should be better than ISO class 5 (see ISO 14644-1). A clean booth should have a local exhaust system.

7.4 *VPD Box* — See ¶ 5.2.2.

7.5 *Automatic Scanning Equipment* — The automatic scanning equipment should have mechanism to hold and scan a scanning solution droplet. Scan of a droplet can be carried out by manual operation instead of the automatic equipment.

7.6 *Tweezers: Vacuum Tweezers and Manual Tweezers* — Particulate emission from the tweezers should be low.

7.7 *Micropipette* — A micropipette should be validated according to ISO 8655-2 and ISO 8655-6.

8 Reagents and Materials

8.1 *Ultra Pure Water* — Ultra pure water containing less than 1 pg/mL of each of the impurities (i.e., sodium, magnesium, aluminum, potassium, calcium, chromium, manganese, iron, cobalt, nickel, copper, and zinc) is used. This is as per ISO 17331.

8.2 *Ultra Pure Acid* — Acid for the scanning solution (e.g., hydrofluoric acid and hydrogen peroxide) containing less than 10 pg/mL of each of the following impurities: sodium, magnesium, aluminum, potassium, calcium, chromium, manganese, iron, cobalt, nickel, copper, and zinc, should be used.

8.3 *Hydrofluoric Acid for VPD Process* — The purity of hydrofluoric acid could be degraded to less than 100 pg/mL for each of the impurities such as sodium, magnesium, aluminum, potassium, calcium, chromium, manganese, iron, cobalt, nickel, copper, and zinc, because the hydrofluoric acid vapor used in the VPD process is purified after vaporizing.

8.4 *Commercial Scanning Solution* — Recently, the scanning solution has been commercially traded for silicon wafer surface analysis. When the commercial scanning solution is used, it should contain less than 10 pg/mL of each of the following impurities: sodium, magnesium, aluminum, potassium, calcium, chromium, manganese, iron, cobalt, nickel, copper, and zinc.

NOTE 2: As far as possible, acid of the highest purity should be used for the scanning solution with the aim of decreasing the detection limit.

9 Principle of Collection Method

9.1 Decomposition of Silicon Oxide and Collection of Contamination — In this section, the VPD and DADD methods are described. Each method should be selected on the basis of the purpose and analysis environment. The consistency between both sides is described in Related Information 1.

9.1.1 VPD Method — In the VPD method, silicon oxide is decomposed by exposure to hydrofluoric acid vapor; subsequently, trace metals are collected into a high-purity acid droplet that is scanned completely or through any part of the silicon wafer. The droplet is scanned manually or using automatic scanning equipment. The automatic equipment can be expected to have a better repeatability than the manual collection because of a reduced contamination risk by the operator. Scanning condition such as the volume of the scanning solution, scanning speed, and number of scans required should be optimized by using the intentionally contaminated sample in order to satisfy the criterion of the recovery rate. The schematic illustration of the VPD method is shown in Figure 3.

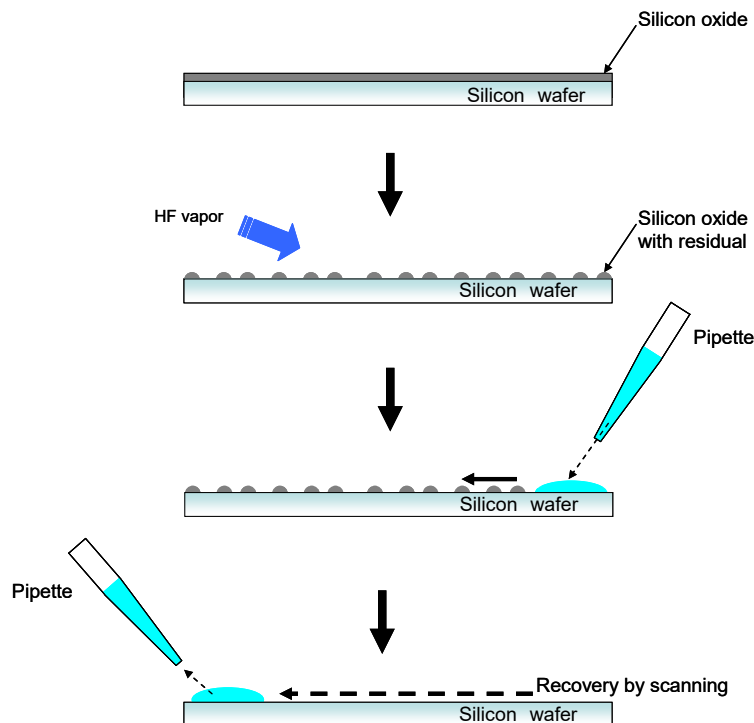


Figure 3
Outline of Sample Preparation in VPD Method

9.1.1.1 Preparation of Scanning Solution — Metal impurities are dissolved in the droplet of the scanning solution on the silicon wafer surface after the VPD process. In this process, noble metals such as copper, which have weak ionization tendencies, is easy to re-adhere to the silicon surface because of the oxidation-reduction interaction. Therefore, a mixture of acid and an oxidizing agent should be used as the scanning solution in order to improve the recovery rate by accelerating the ionization of copper with a high oxidation-reduction voltage of the solution. The mixture of several percent hydrofluoric acid and several percent hydrogen peroxide, or the mixture of several percent hydrofluoric acid and several percent nitric acid is a representative example of the scanning solution. For example, a mixture of 2% hydrofluoric acid and 2% hydrogen peroxide is used for the collection of iron and nickel in ISO 17331. This composition was also used in the review of current technology in this Guide, and the difference of measurement values of iron among the sites was small (see Related Information 1). However, in the measurement of noble metals such as copper, the scanning solution composition should be optimized carefully. In some cases, increase in the concentration of an oxidizing agent such as hydrogen peroxide or nitric acid may be required, or a change in other analysis conditions such as scanning speed may be required. Suitable analysis conditions depend on the automatic scanning system, wafer surface condition, etc. The composition of the scanning solution should be optimized to satisfy

a defined criterion for the recovery rate of each measurement elements. The criterion for recovery rate is fulfilled if the recovery rate is in the range of 75% to 125%. The procedure for the determination of the recovery rate is described in Appendix 1. The scanning solution can be prepared from commercial ultra-high purity reagents. Contamination control for a clean room, vessels, and equipment should be performed routinely. In order to determine the background level of trace metal contaminants, their amounts in the scanning solution should be evaluated by the ICP-MS technique in the same manner as this Test Method.

NOTE 3: The composition of the scanning solution is an important parameter for the comparison of measurement data between facilities. It should be referred to if necessary.

9.1.2 *DADD Method* — In the DADD method, silicon oxide is decomposed using a high purity acid droplet. Silicon oxide and trace metals are simultaneously collected. In general, the droplet is scanned on the entire wafer surface after decomposition. The schematic of the DADD method is shown in Figure 4.

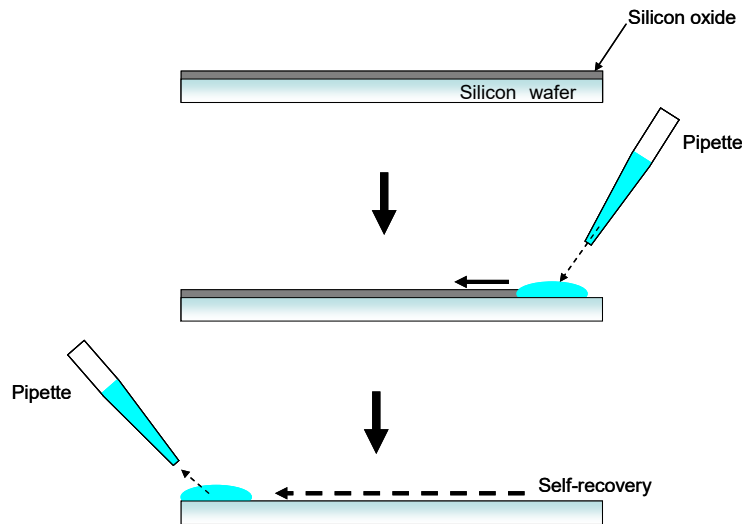


Figure 4
Outline of Sample Preparation in DADD Method

9.1.2.1 *Preparation of Scanning Solution* — The scanning solution for the DADD method should be composed of hydrofluoric acid and other acids because of the decomposition of silicon oxide. The concentration of hydrofluoric acid should be optimized along with the thickness of silicon oxide. Preparation except the concentration of hydrofluoric acid is same as ¶ 9.1.1.1.

10 Procedure

10.1 VPD Method

10.1.1 *Environment* — The operation consists of sample preparation and measurement by using ICP-MS. Sample preparation should be carried out in a clean draft having a local exhaust system. The wafer should be placed in the environment that is better than ISO class 5 (see ISO 14644-1) during sample preparation, in order to eliminate contamination from an environment. Furthermore, the sample solution should be placed in an environment that is better than ISO class 5 during a measurement by ICP-MS.

10.1.2 *Wafer Handling and Storage* — The sample wafer should be handled with gloves by using metal-free tweezers or vacuum tweezers to avoid contamination and direct contact. The sample wafer should be stored in closed containers (e.g., wafer shipping box).

10.1.3 *Decomposition of Native Oxide and Thermal Oxide* — Take hold of a silicon wafer backside by a vacuum tweezer. Place the silicon wafer in the VPD box under clean environments such as the interior of a clean draft. Expose the surface of the silicon wafer to hydrofluoric acid vapor till native or thermal oxides were completely decomposed. Determine a processing time for complete decomposition of silicon oxides in advance.