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# Development of Intentional Contamination in Iron by Bath for Silicon Wafers and Evaluation of VPD-Bulk and LPD-Bulk for Metallic Contaminants Analyses by ICPMS

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**Keywords:** Intentional contamination, LPD-Bulk-ICPMS, VPD-Bulk-ICPMS, SC1, metallic contaminants.

**Abstract** This paper offers a preliminary study for the analysis of metallic contamination on front-end patterned wafers obtained by two different techniques based on the etching of the whole patterns, LPD-Bulk and VPD-Bulk coupled with an ICPMS. To elaborate the analysis of patterned wafers, methods were first verified and optimised on reference Si wafers. Both techniques are complementary methods for the etching of wafers. LPD-Bulk enables a fast etching of several micrometres of Si but with less precision than VPD-Bulk, which is more adapted for the etching of layers thinner than 1 micrometre. The intentional contamination in SC1 and H<sub>2</sub>O bath of monitoring wafers showed that contamination in H<sub>2</sub>O is better controlled due to the absence of chemical reactions, competition between oxidation and etching processes occurring during SC1. And diffusion of contaminants at the tested temperatures from 20°C to 80°C, does not occur. Heat treatment should be applied to allow the diffusion of metallic contaminants in the bulk of the wafers.

## Introduction

The complexity of integrated circuits has increased in a way that makes the presence of metallic contaminants an important topic in microelectronics. Metallic contamination is unavoidable because the fabrication processes or human activity can be sources of contamination. Metallic contamination can occur at each step during a flow in cleanroom, inducing detrimental consequences on the electrical properties of the devices, depending on their location, quantity and nature. Generally, metallic contamination of processed wafers is indirectly analysed via the control of the process tools by using smooth reference silicon (monitoring) wafers, which validates the absence of contamination during all manufacturing steps. Knowing the complexity of the integrated circuits, this approximation seems to be very simple, so the analysis of front-end patterned wafers becomes more than necessary. Currently, it is not possible to analyse patterned wafers with existing analysis techniques such as Total X-Ray Fluorescence (TXRF), Vapor Phase Decomposition – Inductively Coupled Plasma Mass Spectroscopy (VPD-ICPMS) or Liquid Phase Decomposition – ICPMS (LPD-ICPMS). All those techniques are well-adapted for smooth wafers but have limited application for the analysis of patterned wafers due to the surface roughness [1, 2]. Thus, it is necessary to develop a method for the qualitative and quantitative analysis of front-end patterned wafers. One possible solution is to add a step based on the complete etching of patterns to make the final surface smoother and to enable the analysis. The etched thickness should be around the thickness of the patterns and therefore should be well mastered, with layers in Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub> or Si that could involve changes in chemistry compared to the surface analysis. Two types of etching techniques are possible: LPD-Bulk (manual one at CEA) and VPD-Bulk (automatic one at STMicroelectronics) both followed by ICPMS analysis.

To study the quantification of metallic contaminants of patterned wafers, reference wafers with selected compositions and levels of contamination are needed. Intentional contamination of monitoring wafers is usually achieved by spin-coating, a method using centrifugal force to deposit a thin film evenly. But this well-controlled method may not be suitable for all types of patterns. The roughness induced by the patterns can prevent the chemical solution from being deposited homogeneously on the surface of the wafer as well as inside the patterns. Therefore, contamination method based on the soaking of wafers in a bath needs to be developed. It should allow homogeneous contamination of patterned wafers, on the surface and inside the patterns.

This paper deals with the development and understanding of bath contamination and the control of the etched thicknesses by VPD-Bulk and LPD-Bulk on monitoring Si wafers. The developed method will be tested on patterned wafers in a further step.

## Methodology

Different chemical baths used for intentional contamination of Si wafers were studied in the past, such as H<sub>2</sub>O, SC1 (Standard Clean 1), Caro's acid, SC2 (Standard Clean 2) and HF [3]. It was found that SC1 enables the deposition on silicon surface of metallic contaminants that precipitate in this media, like Fe. In addition, H<sub>2</sub>O bath enables better deposition than SC1 of soluble metallic elements like Cu and Ca. Fe and Al can also be deposited in a H<sub>2</sub>O bath, but at a lower concentration than in SC1 bath.

In this study, the first selected contaminant is Fe (10<sup>6</sup> ppb) in HNO<sub>3</sub> 5%, a mono-elemental solution supplied by Alfa Aesar. Si wafers of 200 mm diameter, p-doped and oriented (100) were treated by a HCl/O<sub>3</sub> ultrasonic clean before intentional contamination.

SC1 composed of NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O bath was used in a ratio of (1:1:5), the chemicals used are NH<sub>4</sub>OH, 29%, SULSI, CMC Materials and H<sub>2</sub>O<sub>2</sub>, 30%, ULSI, Technic Inc. The bath was heated successively at 20, 50 and 80°C. For each temperature, contaminations were made at 1, 10, 100 and 1000 ppb, wafers were treated for 5 min and then rinsed and dried. The used chemicals have the particularity of etching the silicon dioxide with NH<sub>4</sub>OH and oxidizing silicon with H<sub>2</sub>O<sub>2</sub>, according to the following equations [4]:

Etching of silicon dioxide:



Oxidation of silicon:



For the H<sub>2</sub>O bath (de-ionized water, pH = 6.5 ± 0.1 at 20°C), it was heated successively at 20, 50 and 80°C. For each temperature, contaminations were made at 1, 10, 100 and 1000 ppb, wafers were treated for 5 min and then rinsed and dried.

Contaminants concentrations were determined by TXRF in sweeping mode (Rigaku, TXRFV310) which provides surface concentration and local information. The X-ray source is produced by a tungsten anode, the energy and the angle of the incident rays depend on the analysed element. Here, they are respectively around 9.7 keV and 0.1 degree. VPD-ICPMS (Rigaku, V300 – Agilent, 8800 ICPMS) confirmed the surface concentrations measured by TXRF.

VPD-Bulk-ICPMS (IAS25 Expert<sup>TM</sup> - Agilent 8900 ICPMS) and LPD-Bulk-ICPMS (manual - Agilent 7900 ICPMS) techniques are compared. For the determination of the etch rate for VPD-Bulk, ozone (O<sub>3</sub>) is generated from O<sub>2</sub> gas by an internal electric generator at a flow of 2.5 L/min. Alongside O<sub>3</sub>, HF gas is generated from HF 49%, S2ULSI, by a micro-flow nebulizer and conveyed via a flow of N<sub>2</sub> at 1L/min. The etch time is chosen from 375s to 1500s. For LPD-Bulk, a solution of HF 38% (FUJIFILM Wako Pure Chemical Corporation, S3ULSI) and HNO<sub>3</sub> 69.5% (S2ULSI, distilled from HNO<sub>3</sub> 69.5% CMC Materials SULSI) is used. The volume of the solution depends on the size of the wafer and is around 1mm thick to cover the whole surface. Etch rate was determined by variation of the etch time from 10s to 100s.

## Results & Discussion

### VPD-Bulk & LPD-Bulk etching

VPD-Bulk and LPD-Bulk are the techniques used for the preparation and the collection of metallic contaminants for ICPMS analyses.

Fig. 1 illustrates the steps of VPD-Bulk-ICPMS. The wafer is processed in the VPD chamber (1 & 2), then contaminants are collected with a chemical droplet (HF/H<sub>2</sub>O<sub>2</sub>) by scanning the surface of the wafer (3) and finally, the droplet is conveyed to the ICPMS for analysis.

In the VPD chamber, ozone (O<sub>3</sub>) gas oxidises silicon and HF etches SiO<sub>2</sub>. By variation of the etch time, it is possible to know the etched thickness as a function of time, Fig.2 (measured by Model-Based Infrared Reflectometry, Semilab AMS, IR3100). No saturation nor decrease was observed and the determined etching rate is 0.6 nm/s with an error of 2%.

Different HF gas flow at 1.5, 1.75 and 2 L/min were tested. The etching time was 1500 s and O<sub>3</sub> flow was 2.5 L/min. No change of the etched thickness was observed which stays around 1 μm. Additionally, with an etching time of 1500 s and HF flow of 1 L/min, different O<sub>3</sub> gas flows were tested at 1.2, 1.5, 3 and 3.5 L/min. No influence on etched thickness was observed, it remains around 1 μm. However, it was observed that at O<sub>3</sub> = 3.5 L/min flow, the surface becomes hydrophilic. This can be explained by the fact that the balance between etching and oxidation was disturbed. Such high flow of O<sub>3</sub> leads to a domination of oxidation process over etching.

As the etched thickness does not increase over 1 μm at an etch time of 1500 s with various HF/O<sub>3</sub> flows, the parameters used for the determination of the etch rate are optimal (HF/N<sub>2</sub> flow = 1 L/min and O<sub>3</sub>/O<sub>2</sub> flow = 2.5 L/min).

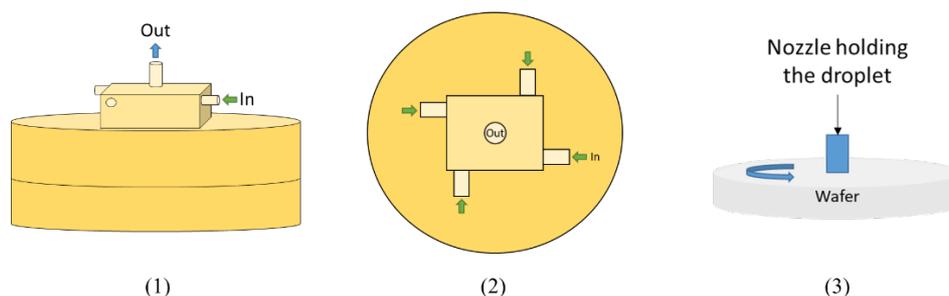


Figure 1. (1) VPD chamber side-view, (2) VPD chamber viewed from above, (3) collection of contaminants by a HF/H<sub>2</sub>O<sub>2</sub> droplet.

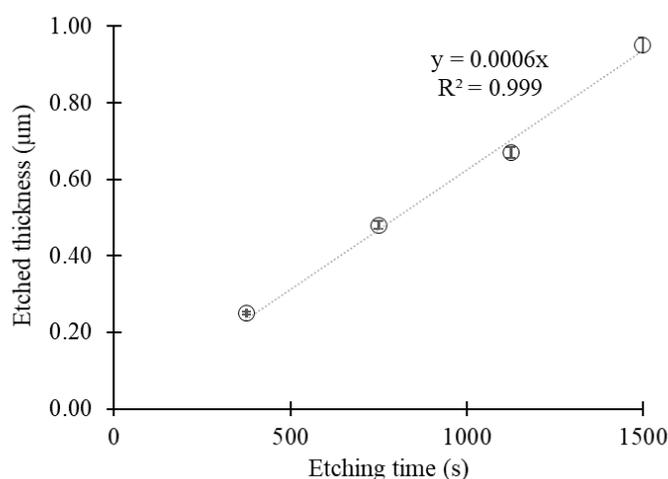


Figure 2. Etch rate for VPD-Bulk, measured by model-based infrared spectroscopy.

LPD-Bulk uses HF/HNO<sub>3</sub> solution. HF etches SiO<sub>2</sub> and HNO<sub>3</sub> oxidises Si. This manual method uses a PTFE mould adapted to the size of the wafer where it is held by the edges as shown in Fig. 3 (1). The HF/HNO<sub>3</sub> solution is poured on the Si wafer to cover the whole surface for a homogeneous etching (2) and the reaction occurs for a given time depending on the desired etched thickness (3). Then, the solution is sampled for ICPMS analysis (4). The etching at several reaction times from 10s

to 100s (Fig. 4) was carried out to determine the etching rate. Unlike VPD-Bulk, the etched thickness as a function of time is not linear. The etching is fast at the beginning and slows down from 75s. During the etching an orange-brownish gas is formed, the amount of gas decreases as the etching time increases. The reaction might slow down as reactants are consumed. As the method is manual, an error between 3% and 7% is found.

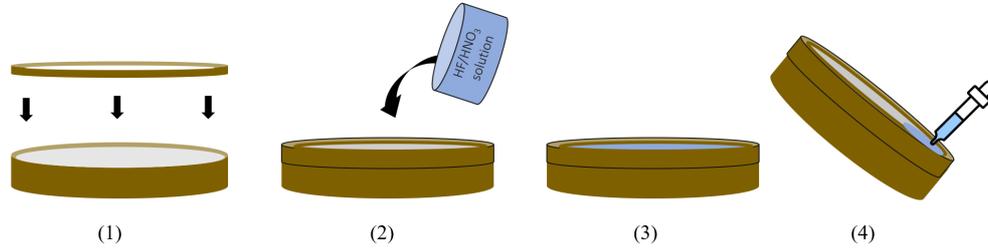


Figure 3. LPD-Bulk steps.

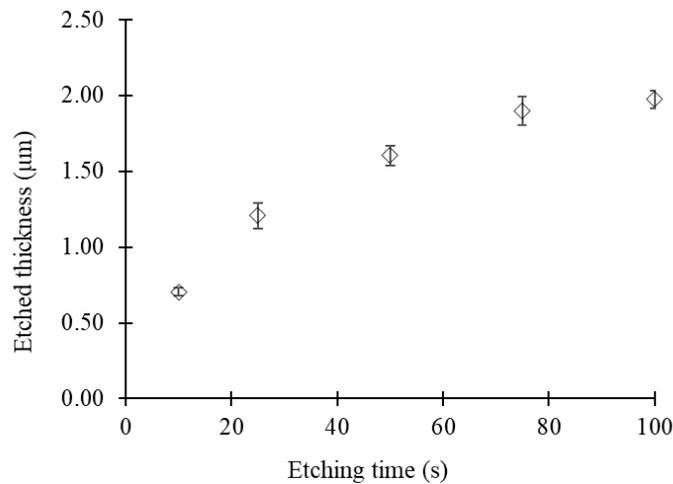


Figure 4. Etch rate for LPD-Bulk, calculated from the weight of the wafer.

### Iron contamination using SC1 & H<sub>2</sub>O baths

Fe surface concentrations are found to be similar for contamination in H<sub>2</sub>O and SC1 baths when the bath is contaminated at 1 and 10 ppb (Fig. 5). There is no influence of temperature on the surface concentration in H<sub>2</sub>O. However, for SC1 bath, an increase of surface concentration with temperature is observed. At 100 ppb, a change occurs in both solutions. The surface concentration saturates in H<sub>2</sub>O bath at 20°C, while the increase of temperature enables higher surface concentration of contamination. In SC1, the surface concentration saturates in the bath heated at 80°C, the same is observed at 1000 ppb. Moreover, the increase of temperature in the presence of contaminants induces bubbling and evaporation of the bath. An additional contamination in SC1 was conducted at 100 and 1000 ppb directly heated at 80°C, surface concentrations are ten times superior to the previous values. L. Mouche *et al* explains the difference of surface concentration in SC1 and H<sub>2</sub>O by a difference in ionic strength. However, the influence of temperature and pH were not discussed.

As the surface of the wafer is covered by SiO<sub>2</sub>, Si-OH groups are formed when a wafer is immersed in an H<sub>2</sub>O bath. A competition between metallic ions and hydrogen ions occurs. The higher the concentration of H<sup>+</sup>, the smaller the concentration of metal is deposited [5]. Thus, pH of the bath influences directly the deposited ions. The rise of temperature leads to the formation of more H<sup>+</sup> (and HO<sup>-</sup>), so the concentration of M<sup>+</sup> on the surface should decrease.

However, at small concentration of contamination (1 and 10 ppb), temperature does not influence the surface concentration. While at high concentration of contamination (100 and 1000 ppb), the surface concentration saturates for contamination at 20°C from 100 ppb and at 50°C from 1000 ppb. Fe ions might have reached the limit of adsorption site in competition against hydrogen ions and the increase of temperature would have favoured the deposition of Fe.

In SC1, changes in temperature, pH, and the presence of contaminants was proved to influence the stability of the bath [6]. It showed that the increase of temperature speeds up the decomposition of H<sub>2</sub>O<sub>2</sub> and induces the evaporation of NH<sub>4</sub>OH. At high pH, the decomposition of H<sub>2</sub>O<sub>2</sub> is also faster. Additionally, the operating time is relatively long, the contaminations were performed by progressively rising the temperature of the bath, which contributes to decreasing the reactivity of the bath. Also, the presence of metallic contaminants catalyses the decomposition, especially with Fe. Altogether, the equilibrium of silicon dioxide etching by NH<sub>4</sub>OH and silicon oxidation by H<sub>2</sub>O<sub>2</sub> is shifted as their respective concentrations evolve during the operating time. According to Lim [7], if the oxide layer is thinner than 1.1 nm, the oxidation phenomenon dominates. With thicker oxide layers, etching phenomenon dominates.

A measure of the native oxide thickness before SC1 treatment and the oxide formed by the SC1 treatment at 80°C was performed by ellipsometry. One bath was contaminated with iron at 10 ppb and the other one without contamination. As seen in Table 1, no differences are observed for non-contaminated or contaminated baths. The oxide thicknesses measured are of about 1.0-1.1 nm, exactly the limit thickness mentioned by Lim. Our experiments do not allow to state on the dominant reaction.

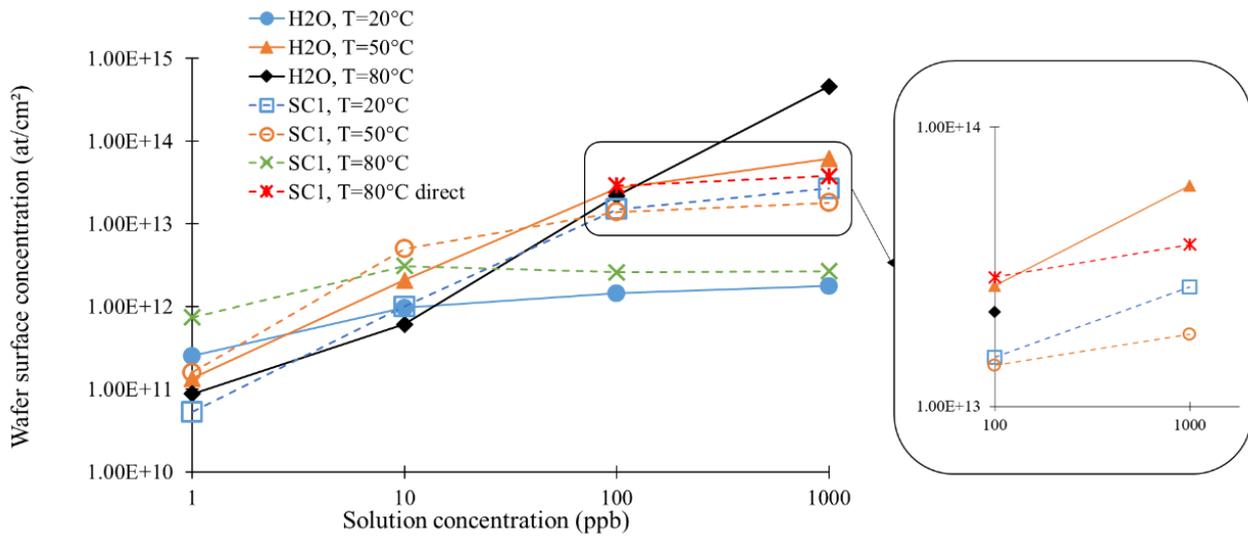


Figure 5. Surface concentration of iron determined by TXRF as a function of the level of contamination added to the SC1 bath 1:1:5 and the H<sub>2</sub>O bath for different temperatures, treatment time of wafers in the bath is 5 min.

Table 1. Oxide thickness measures by ellipsometry before SC1 treatment and after SC1 treatment heated at 80°C.

Oxide thickness (nm)	Not contaminated SC1		Iron contaminated SC1 (10 ppb)	
	Before	After	Before	After
	1.2	0.9	1.2	1.1

A VPD-ICPMS analysis followed by a LPD-Bulk-ICPMS analysis was carried out on the wafers contaminated in SC1 bath heated at 80°C with a contamination at 1, 10, 100 and 1000 ppb. These are the same wafers from Fig.5 where a saturation of surface concentration was observed for contamination above 10 ppb.

To ensure that the LPD-Bulk-ICPMS only gives the concentration found in the bulk and not on the surface, three consecutive collections were done with VPD-ICPMS. The Collection Efficiency (C.E) of VPD-ICPMS was calculated with the following equation:

$$C.E = \frac{C_1}{\sum C_i} * 100. \tag{4}$$

C<sub>1</sub> is the concentration of the first collect.

C<sub>i</sub> represent de concentration of the i<sup>th</sup> collect, here i = 3.

TXRF and VPD-ICPMS gave similar surface concentrations (Table 2), with a E.C superior to 96%. and LPD-Bulk-ICPMS did not detect any trace of Fe in the first two micrometres. Which confirms that the saturation is caused by the decrease of the reactivity of the bath, and that iron did not diffuse into the Si bulk and only stayed in and on the surface of the silicon oxide layer. Diffusion would have been highly unlikely at this temperature [8].

Table 2. Iron concentration of intentionally contaminated wafers analysed by TXRF and VPD-ICPMS, ND = Non-detected, the concentration is under the limit of detection. \*wafer directly contaminated at 80°C, \*\* contamination of the analyte during the handling.

Contamination concentration (ppb)	TXRF (E+10 at/cm <sup>2</sup> )	VPD-ICPMS (E+10 at/cm <sup>2</sup> )			
		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C.E (%)
1	65	55	0.09	0.13	99.6
10	310	230	0.85	ND	99.6
100	260	220	1	0.5	99.3
1000	267	300	7.9	4.4	96.1
1000*	3800	3300	9.7	63**	97.8

## Conclusion

The bulk etching feasibility was demonstrated on non-patterned silicon wafers. VPD-Bulk allows a more precise control of the etched thicknesses since the etching rate is lower with this automatic system, 0.6 nm/s. However, it is not adapted for the etching of Si layers thicker than 1 µm. While LPD-Bulk is better suited for deeper etching but it is difficult to master since the etching is faster and the process is manual.

Bath contamination by SC1 is limited in time as temperature and the presence of metallic contaminants catalyse the decomposition of H<sub>2</sub>O<sub>2</sub>, leading to the depletion of the bath reactivity. In the case of intentional contamination, the oxidation is preferable over etching. But the study of the oxide thickness formed by SC1 in these experimental conditions does not show a preference of oxidation or etching. Concerning H<sub>2</sub>O bath, it does not induce chemical effect constraints and can contaminate wafers at higher and similar contamination levels to SC1. In terms of contamination efficiency, handling safety and the environment, H<sub>2</sub>O bath is a more suitable option.

VPD-Bulk, LPD-Bulk etching and bath contamination were performed on smooth silicon wafers. Other contaminants such as Ni and Cu will be tested before adapting the protocol to patterned wafers. Moreover, the contamination remains on the surface, so ways to favour diffusion of the contamination into the bulk must be found, for example a heat treatment of the wafer after contamination.

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