# Predictive analysis of ceramics holders for $WF_6$ CVD processes

Laurent Doyen, Romain Joly, Maryse Bellmunt
*Air Liquide Electronics, Balazs™ Analytical Services, 224 Bd J Kennedy F- 91105 Corbeil-Essonnes, France*

Fuhe Li
*Air Liquide America, Balazs™ Analytical Services, 46409 Landing Parkway, Fremont CA 94538-6506, USA*

*Hervé Dubus*
*Didier Bourdenet*
*ST Microelectronics, ZI de Rousset BP2 13106 Rousset Cedex, France*

**Abstract**

Ceramics parts are commonly used in Semiconductor manufacturing as wafer holders in CVD processes. In the frame of cost reduction programs and contamination control, some S/C manufacturers expressed a need for non-destructive analytical technique able to characterize the contamination level of these ceramics parts. This paper describes Air Liquide's analytical solution to such issue for ceramics parts used in $WF_6$ CVD processes. Several analytical techniques are compared to consolidate the study.

The proposed analytical procedure turns out as a relevant tool for ceramics clean procedures qualification as well as a determining factor for predictive ceramics parts exchange.

## Introduction

One of the most sensitive step regarding Chemical Vapour Deposition (CVD) processes is the chamber clean run frequently between batches of thin film deposition steps. The chamber clean step is mandatory to eliminate any particle contaminants coming from sticking materials accumulated during the deposition step onto the chamber walls made of ceramics material. The common method used to evaluate a cleanliness level of a CVD chamber is generally based on particle monitoring on Silicon wafers using on-line defectivity inspection tools.

Moreover, the ceramics parts used in CVD chambers are cleaned using an external cleaning process on a regular basis, generally as a function of a given amount of wafers processed. Obviously, the goal of these clean processes is to remove the contaminants present onto the ceramic surface with a minimum degradation of the ceramic material. In order to assess both the cleanliness level of the ceramics parts as well as the clean process efficiency, a need is expressed for a direct and non destructive analytical method.

Investigations for the design of the adequate analytical procedure are mainly performed towards three axis which are 1)identify the most relevant parameter(s) reflecting the cleanliness of a ceramics part, 2)find the most adapted and non destructive analytical method to be used to monitor these relevant parameters, 3)compare and confirm analytical results with alternative and complementary techniques. The present work is focused on ceramics parts made of alumina given to at least 99,5% (w/w) purity regarding metallic contamination.

The background information both on CVD and cleaning processes commonly used or recommended helps in selecting the proper analytical techniques. Since this work is mainly focused on parts used in CVD processes using $WF_6$ chemistry, techniques able to identify and quantify metals and particles are of choice. Inductively coupled plasma mass spectrometry (ICP-MS) is selected for trace metal analysis. It is used in two different ways, one after liquid extraction, the other one after laser ablation (SARIS) of the solid material to be analyzed. In standard ICP-MS analysis, solutions are nebulized into an argon plasma. The contaminants dissolved in the solutions are vaporized, atomized, ionized, and extracted into a mass spectrometer for analysis. One of the advantages of ICP-MS is that a wide range of elements in the periodic table from Lithium to Uranium can be identified and quantified at one time to parts per trillion levels. Depending on the liquid extraction protocol, this method can be non destructive for the ceramic material to be analyzed. The disadvantage in such analysis is that it requires a liquid extraction to transfer the contamination from the solid to the liquid phase. It is therefore submitted to yield considerations depending on extraction protocol. Three liquid phase protocols are selected and compared. The choice is based on the industrial clean process used for parts cleaning, literature[1-3] and ceramic supplier recommendations.

SARIS-ICP-MS is based on the same principle for the ICP-MS part. But instead of analyzing liquid samples, the laser ablation performed on the solid surface will directly sputter and vaporize the solid surface[4]. The extracted solid material is then introduced to the argon plasma of the ICP-MS and undergoes the same process than for standard ICP-MS analysis. The advantage of this technique is that there's no intermediate media for metal analysis and metallic contaminant depth profiles as the solid is undergoing the laser ablation process can be performed as well. The drawbacks are essentially due to the fact that it is a sputtering and local analysis, the laser beam is only 2 mm² wide and the chamber is too small to load an entire ceramic piece, for these reasons it is a destructive analytical method. Finally, the quantification of elements is also tedious due to the lack of standard materials comparable to the solid matrix analyzed currently in this paper.

Particle levels after liquid extraction can also be candidate as a relevant indicator of the characterization of ceramics parts. Particle counting techniques are able to size and quantify the contaminants present onto the ceramics surface. Particles analyzed are ranging from 0,2µm to 2µm. This kind of technique has the advantage to give quantified results easily comparable between samples, non destructive depending on the extraction protocol used. But it shows the same drawback related to liquid extraction than for ICP-MS method as well as no information given on the nature of the particles counted. The same extraction protocols than for ICP-MS analysis are investigated using this technique.

Finally, in order to assess the solid material integrity depending on the liquid extraction method used, microscopic observations of the solid surface using Scanning Electronic Microscopy (SEM)

are performed. Due to the chamber size, ceramic samples must be once again broken into small pieces, it is therefore a destructive analysis.

The combination of these analytical techniques and extraction protocol will permit to define the adapted analytical procedure to be used in the field to characterize routinely the cleanliness level of ceramic parts in a non destructive way as well as to identify the most efficient industrial cleaning process.

## Experimental

The chosen three extraction protocols to be evaluated are the following: extraction with peroxide 30% (w/w) for 30 minutes to room temperature; extraction with desionized water (DIW) under ultra-waves at 40kHz for 30 minutes to room temperature; extraction with nitric acid 7% (w/w) to room temperature for 30 minutes. Blank runs are performed using the considered extraction procedure without the ceramic material dipped into.

Particle counting are performed in Air Liquide – Balazs$^{TM}$ Analytical Services' Europe Laboratory using a Hiac/Royco Microcounter analyzer on extracted solutions of ceramic parts. Particle size ranges from 0,2µm to 2µm. Results are expressed in particle/mL of wet solution as an average of three replicas with the same 500mL wet solution subtracted by the average of five blank runs.

Quantification of metallic impurities in 500mL extracted solutions are performed in Air Liquide – Balazs$^{TM}$ Analytical Services' Europe Laboratory on a HP4500 ICP-MS. Results are expressed as an average of three runs in ng/g or ng/piece of extracted ceramic material subtracted by the average of three blank runs.

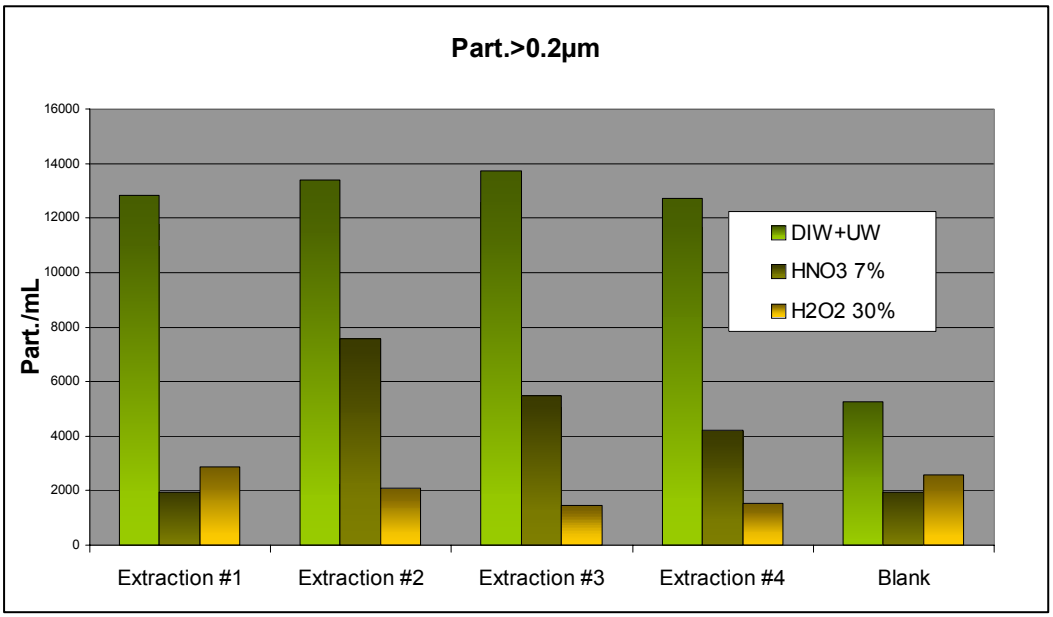
All SARIS measurements in this study were performed at the Air Liquide – Balazs$^{TM}$ Analytical Services' Fremont Laboratory. The ceramics were directly analyzed using the laser ablation ICP-MS system without going through any wet chemical dissolution steps. A short-pulsed and high power UV laser with a 110 µm spot size was used to sputter or ablate the ceramic materials. The sampling areas used for depth profiling and quantitative analyses were 110 µm and 2 mm$^2$ (via rastering technique), respectively. The ablated materials were consequentially analyzed by a Varian Ultramass 700 quadrupole based ICP-MS. Duplicate analyses at different sampling locations for each material were performed and the data averaged.

SEM observations of ceramics surfaces are performed on a low vacuum Hitachi SEM with different magnification ranging for 1:25 to 1:1000 to the operating pressure of $10^{-3}$ torr.

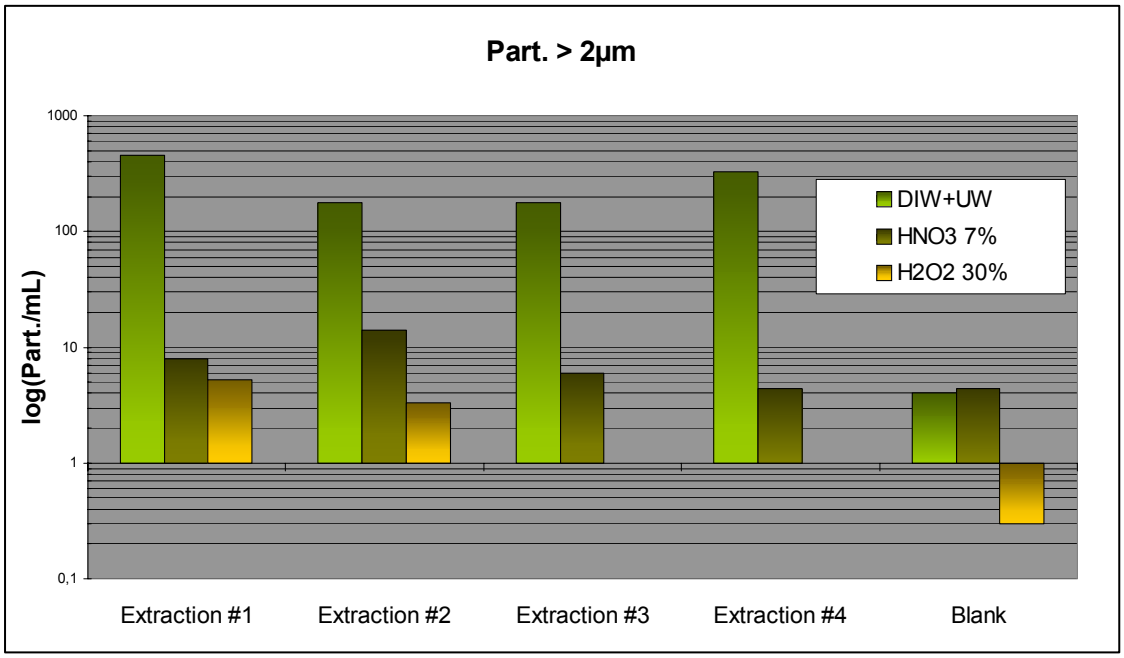
## Discussion

### 1. Wet extractions, comparison of extraction protocols:

This study is performed on a used ring ceramics broken into equivalent pieces to be tested with the three different protocols. Graphs 1 and 2 show the particle levels got with the particle counter after four successive extractions for each protocols. One can notice that the highest particle levels are obtained with the DIW+ultra-waves protocol, which are also fairly consistent over the successive extractions. The lowest levels are obtained with peroxide where the successive extractions are equivalent to the blank quality.

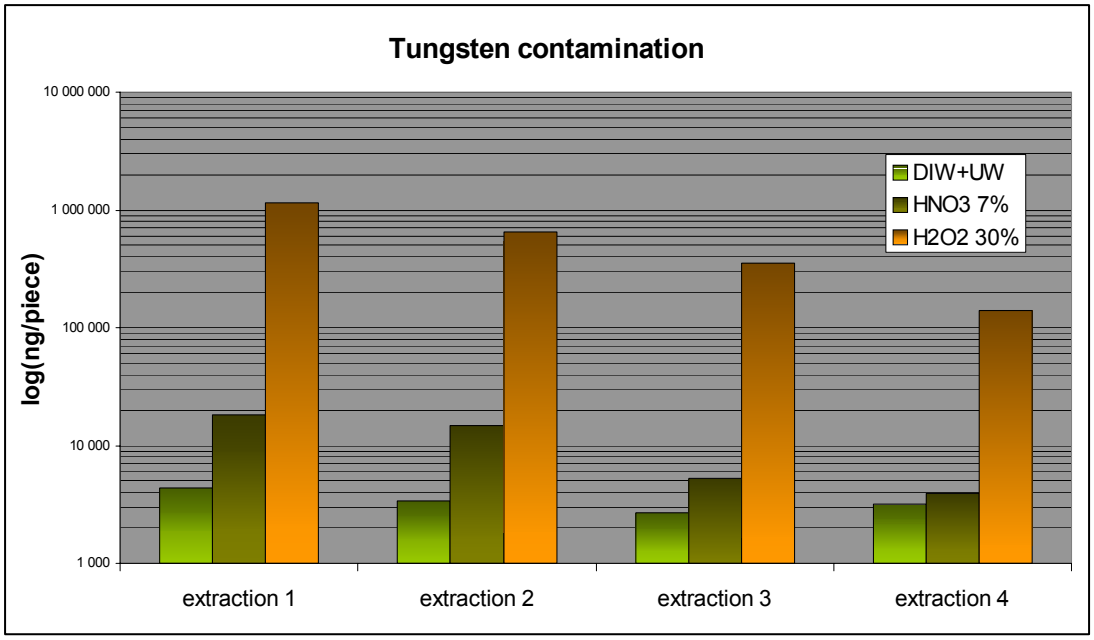



Graph 1 : particle concentration for particle size greater than 0.2µm with four successive extractions

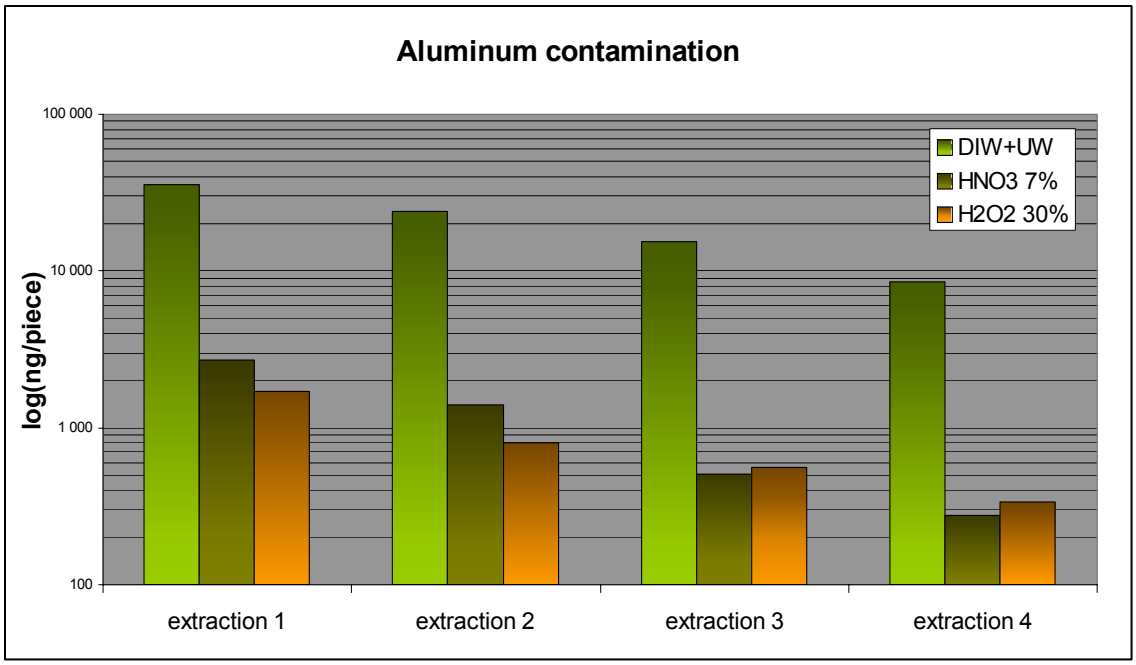



Graph 2 : particle concentration for particle size greater than 2µm with four successive extractions (logarithmic scale)

Using the same extraction solution, ICP-MS is performed concurrently. Graph 3 and 4 give the metallic contamination quantified for the two major elements found which are tungsten and aluminum. Blank values are negligible for both elements because below the ICP-MS quantification limit. Peroxide extraction is the most efficient regarding tungsten recovery whereas it is DIW+ultra-waves for aluminum.

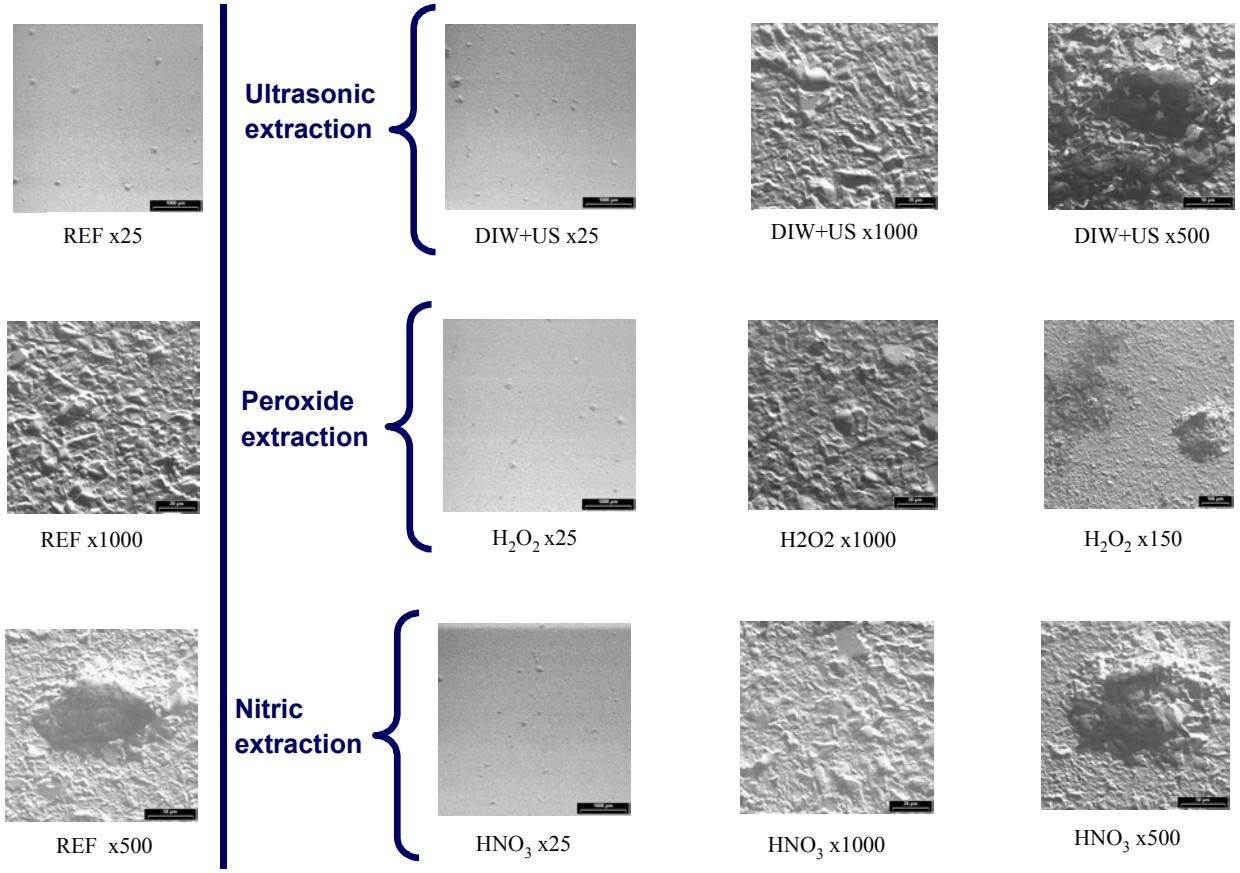



Graph 3: tungsten concentration in ng/piece with four successive extractions (logarithmic scale) for the three different extraction protocols

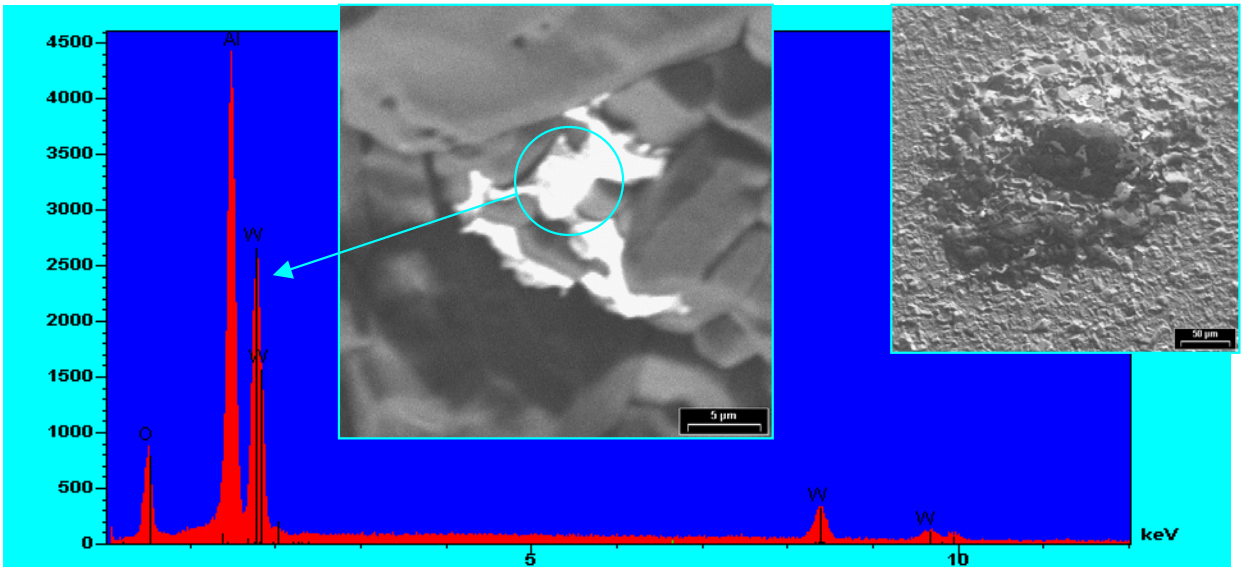



Graph 4: aluminum concentration in ng/piece with four successive extractions (logarithmic scale) for the three different extraction protocols

SEM surface observations are shown in pictures 1 below to various magnifications. The ceramics piece used as reference is the used one prior to any wet extraction. This piece is compared to the other ones after extraction. Nitric and peroxide extraction give equivalent surface morphology whereas DIW+ultra-waves seems to give a surface with wider holes. Some impurities are also identified as tungsten particles onto the ceramics surface thanks to Energy Dispersive X-ray Spectrometry (EDS) as shown on picture 2.

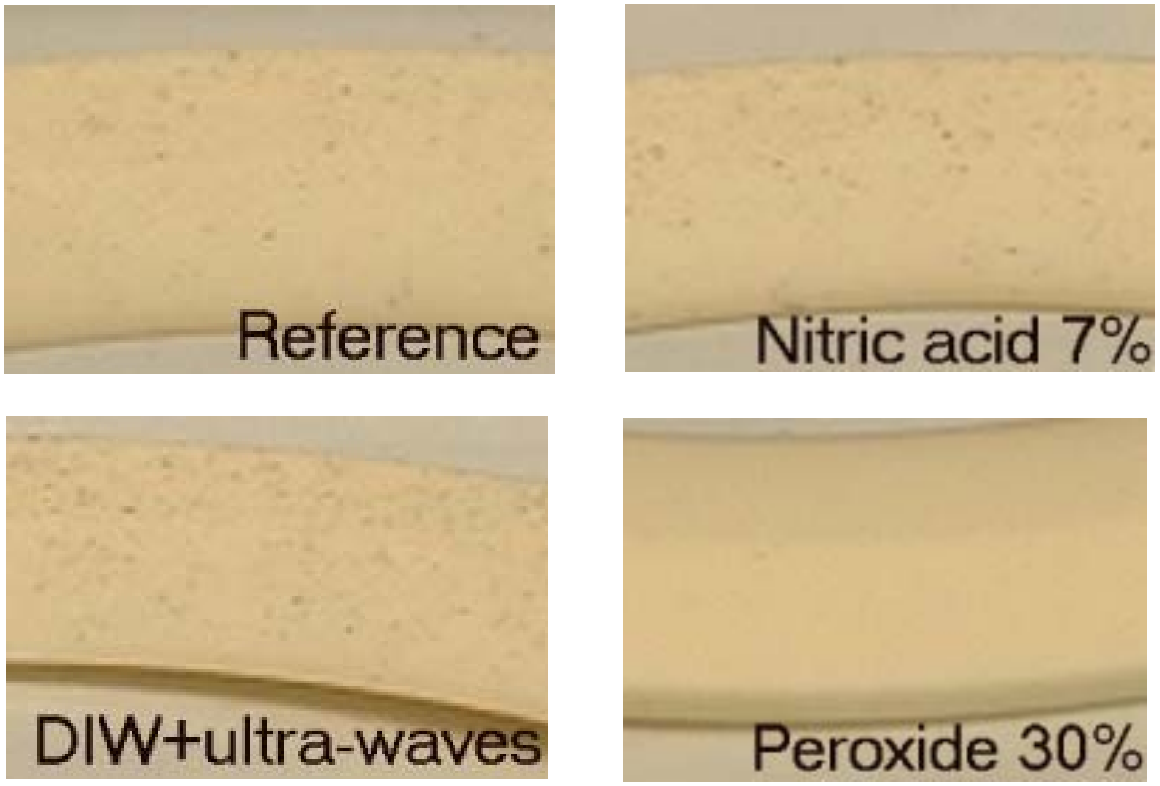



Picture 1: SEM ceramics surface observations to various magnification ranges from x25 to x1000. Reference piece to the left column is compared to the various resulting surfaces after extraction, ranged on rows to the right.




Picture 2: focus on a particle present inside a hole with the corresponding EDX spectrum

Finally, the efficiency of the different extraction protocols can also be assessed by a simple visual inspection of the different pieces compared to the reference one. Picture 3 below gives a comparison between them. Visually, reference piece compared to nitric and DIW+ultra-waves extraction are fairly equivalent whereas peroxide extraction gives a cleaner surface.




Picture 3: visual aspect of the different ceramics: reference vs the three extracted pieces

Globally, the major impurity found on used ceramics is tungsten, based on SEM/EDS analysis as well as ICP-MS after extraction. This is obviously not surprising knowing the process for which these ceramics parts are used for, that is tungsten CVD deposition. The most efficient protocol is the one using peroxide extraction which is by the way one of the cleaning procedure used as an industrial cleaning process, even though four consecutive extractions is not enough to entirely remove all of the tungsten contamination. This is shown by the ICP-MS data as well as the visual inspection. Moreover, this protocol does not seem to alter the ceramics structure as shown by SEM pictures, particle levels equivalent to blank value and the lowest aluminum level which is obviously one intrinsic component of the ceramics material (ceramics made of alumina). On the other hand, the DIW+ultra-waves protocol reveals to be an aggressive treatment based on particle, aluminium levels and SEM inspection. This treatment is also the worst regarding tungsten removal.

As a conclusion, the retained protocol for non-destructive analysis of ceramics parts is ICP-MS analysis after peroxide extraction.

## 2. Evaluation of different industrial cleaning processes:

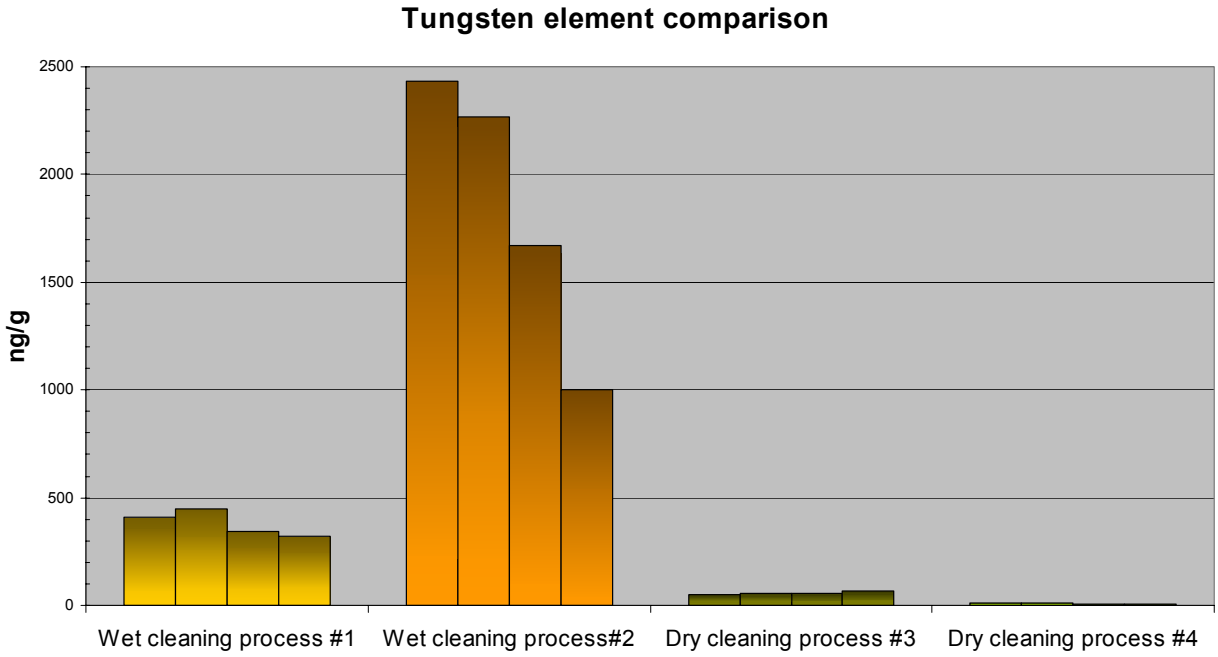
For this study, another used ceramics ring is broken into four equivalent pieces. Each piece undergoes a different cleaning process: pieces #1 and 2 a different wet clean process for each and pieces 3 and 4 a dry clean process to high temperature, also different for each pieces. Due to confidentiality issues, details on the different cleaning processes cannot be revealed into this paper.

These pieces are submitted to different analytical tests which are the retained non destructive analytical protocol here above, SARIS-ICP-MS and SEM/EDS analysis.

Regarding ICP-MS results after peroxide extraction, the most important contaminant found is obviously tungsten as shown in table 1 for clean number 1, as an example. This element is found in important quantity despite the cleaning process of the ceramics parts. Other elements except aluminium, sodium, calcium and potassium which are native impurities of ceramics are pretty close to the reporting limit (RL) of the ICP-MS extraction method. Graph 5 shows a comparison between the different cleaning processes regarding tungsten quantification with four successive extractions for each. These results demonstrate the far better cleaning efficiency of dry clean processes to high temperature compared to the classical wet clean ones.

| Element | RL | Unit | extraction 1 | extraction 2 | extraction 3 | extraction 4 |
|---|---|---|---|---|---|---|
| Sodium | 0,04 | ng/g | 3,14 | < RL | < RL | < RL |
| Magnesium | 0,04 | ng/g | 0,88 | 0,30 | 0,19 | 0,15 |
| Aluminium | 0,04 | ng/g | 6,27 | 3,36 | 2,45 | 1,97 |
| Potassium | 0,04 | ng/g | 1,17 | 0,14 | 0,04 | 0,12 |
| Calcium | 0,04 | ng/g | 3,58 | 1,37 | 0,85 | 0,52 |
| Chromium | 0,04 | ng/g | < RL | < RL | < RL | < RL |
| Manganese | 0,04 | ng/g | < RL | < RL | < RL | < RL |
| Iron | 0,04 | ng/g | 0,04 | 0,10 | < RL | 0,07 |
| Nickel | 0,04 | ng/g | < RL | < RL | < RL | < RL |
| Cobalt | 0,04 | ng/g | < RL | < RL | < RL | < RL |
| Copper | 0,04 | ng/g | 0,27 | 0,10 | 0,09 | < RL |
| Zinc | 0,04 | ng/g | 1,20 | 0,33 | 0,25 | 0,38 |
| Silver | 0,04 | ng/g | 0,13 | 0,04 | 0,04 | < RL |
| Lead | 0,04 | ng/g | 0,07 | 0,05 | < RL | < RL |
| Baryum | 0,05 | ng/g | 0,37 | 0,16 | 0,11 | 0,07 |
| **Tungsten** | **0,03** | **ng/g** | **407** | **448** | **344** | **322** |

Table 1: metallic contamination after peroxide extraction and ICP-MS analysis of a ceramics piece after cleaning process number 1

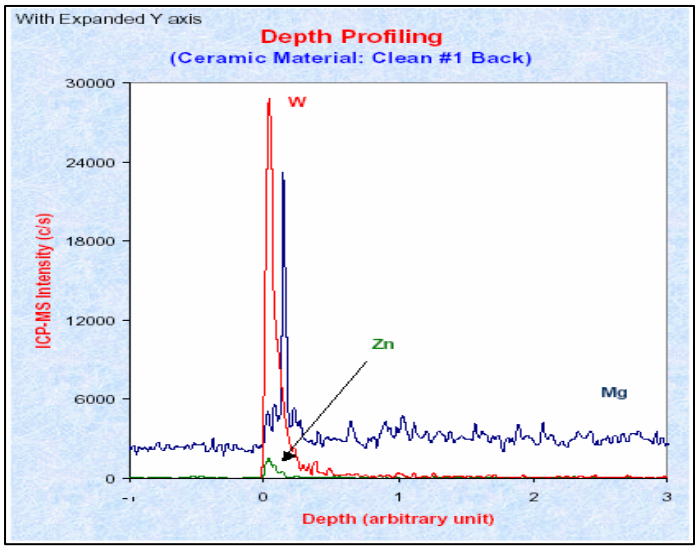



Graph 5: comparison of the four cleaning process with four pieces of ceramics coming from the same ring. Results given in ng/g for tungsten element after peroxide extraction and ICP-MS analysis

Complementary data are obtained thanks to SARIS-ICP-MS measurements on the same four ceramics pieces. Table 2 gives quantitative results for the four pieces, the two first columns give metallic contamination both for front side and backside of the piece of ring for clean process #1 as an example. The same order regarding the clean processes efficiency is respected even though there's much less magnitude between results. This is probably due to the fact that SARIS-ICP-MS quantification is less sensitive than wet extraction ICP-MS analysis. An explanation would lie in the fact that SARIS ablation is a local analysis compared to wet extraction but also because tungsten contamination is really present on the near surface of ceramics as shown on the depth profiles in graph 6. SARIS-ICP-MS gives also an additional information on the location of the contamination which is much more present on backside of the ring, this result is confirmed on all the ceramics pieces studied.

| Element (1E15 at/cm²) | clean 1 (front) | clean 1 (back) | clean 2 (back) | clean 3 (back) | clean 4 (back) |
|---|---|---|---|---|---|
| Sodium | 1,8 | 10 | 5,5 | 5,5 | 1,1 |
| Magnesium | 5,8 | 9 | 9,5 | 4,3 | 6,1 |
| Tungsten | 3,2 | 8,1 | 9,7 | 8 | 1,6 |
| Iron | 2,9 | 7 | 6,9 | 6,1 | 4,1 |
| Potassium | 0,08 | 3 | 0,85 | 0,42 | 0,39 |
| Zinc | 0,23 | 0,5 | 0,54 | 2 | 0,57 |
| Copper | 0,02 | 0,15 | 0,089 | 0,11 | 0,009 |
| Zirconium | 0,007 | 0,074 | 0,023 | 0,03 | 0,016 |
| Manganese | 0,062 | 0,061 | 0,097 | 0,062 | 0,015 |
| Baryum | 0,028 | 0,061 | 0,038 | 0,012 | 0,006 |
| Gallium | 0,015 | 0,021 | 0,019 | 0,015 | 0,014 |
| Strontium | 0,005 | 0,009 | 0,007 | 0,004 | 0,003 |
| Chromium | 0,13 | 0,005 | 0,16 | 0,085 | 0,14 |
| Vanadium | 0,001 | 0,002 | 0,002 | 0,004 | 0,051 |

Table 2: SARIS-ICP-MS quantitative results expressed in 1e15 atoms/cm². Comparison of the four cleaning process with four pieces of ceramics coming from the same ring




Graph 6: SARIS-ICP-MS depth profiling corresponding to the ceramics piece which underwent the cleaning process number 1. Profiles are given for tungsten, magnesium and zinc element. 1 arbitrary unit is estimated to correspond to around 5µm depth.

## 3. Routine characterization in the field:

This study is performed on production ceramics rings with the non destructive analytical procedure as discussed in paragraph 1. Tables 3 and 4 give metallic impurity levels for a new ceramics ring which is not yet used in process, by peroxide extraction followed by ICP-MS analysis and by SARIS-ICP-MS analysis, respectively. Note that SARIS-ICP-MS is not done on a production ring but on a ceramics coupon representative of the considered material. These results are taken as a reference state of ceramics quality and give no tungsten contamination, this is confirmed by both techniques.

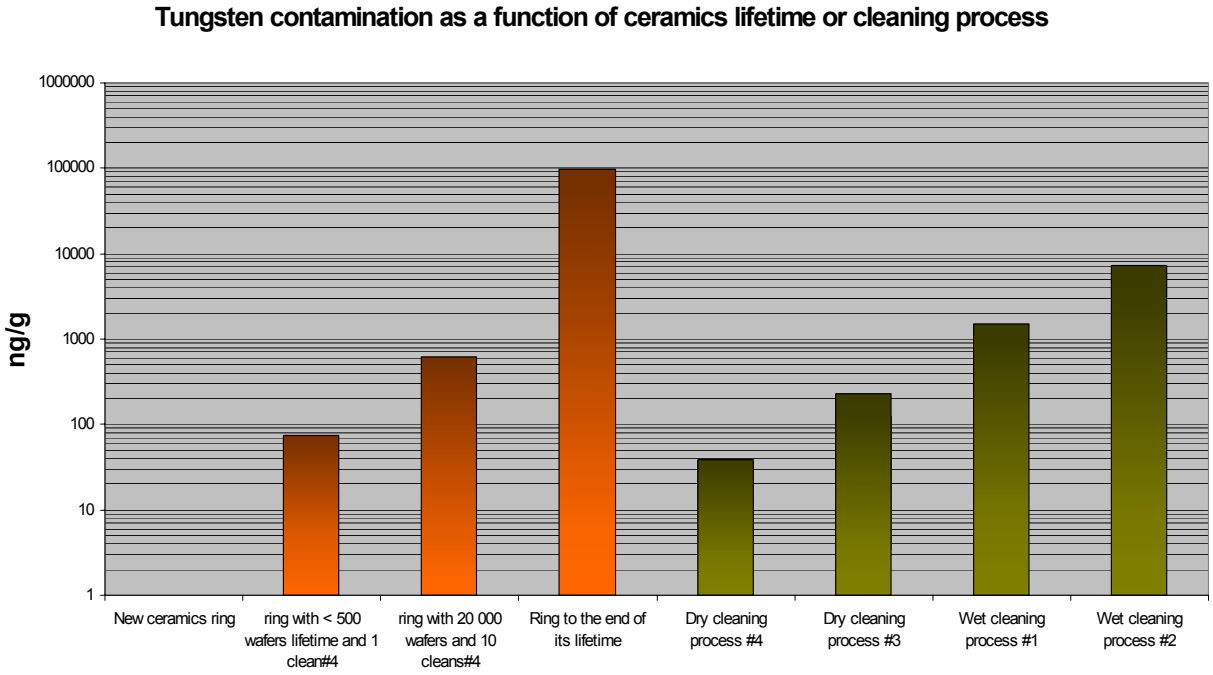
| Element | RL | Unit | extraction 1 | extraction 2 | extraction 3 | extraction 4 |
|---|---|---|---|---|---|---|
| **Sodium** | **2,5** | **ng/piece** | **2089** | **3971** | **1065** | **1399** |
| **Magnesium** | **2,5** | **ng/piece** | 3,9 | 27,2 | < RL | < RL |
| **Aluminum** | **2,5** | **ng/piece** | **2219** | **1420** | **900** | **790** |
| **Potassium** | **2,5** | **ng/piece** | **164** | **1270** | **98** | **61** |
| **Calcium** | **2,5** | **ng/piece** | **1181** | **770** | **148** | **205** |
| **Chromium** | **2,5** | **ng/piece** | < RL | < RL | < RL | < RL |
| **Manganese** | **2,5** | **ng/piece** | < RL | < RL | < RL | < RL |
| **Iron** | **2,5** | **ng/piece** | < RL | < RL | < RL | < RL |
| **Nickel** | **2,5** | **ng/piece** | 9,3 | 8,4 | < RL | < RL |
| **Cobalt** | **2,5** | **ng/piece** | 3,3 | < RL | < RL | < RL |
| **Copper** | **2,5** | **ng/piece** | **88** | **52** | **18** | **26** |
| **Zinc** | **2,5** | **ng/piece** | < RL | 110 | < RL | < RL |
| **Silver** | **2,5** | **ng/piece** | < RL | < RL | < RL | < RL |
| **Lead** | **2,5** | **ng/piece** | < RL | < RL | < RL | < RL |
| **Baryum** | **3** | **ng/piece** | **267** | **91** | **56** | **55** |
| **Tungsten** | **2** | **ng/piece** | < RL | < RL | < RL | < RL |

Table 3: metallic contamination measured by ICP-MS after peroxide extraction for a unused ceramic ring. Results are given for four successive extraction in ng/piece

| Element (1E15at/cm²) | Reference |
|---|---|
| Sodium | 0,068 |
| Magnesium | 4 |
| Tungsten | <0,005 |
| Iron | 0,12 |
| Potassium | 0,31 |
| Zinc | 0,017 |
| Copper | <0,01 |
| Zirconium | 0,045 |
| Manganese | <0,05 |
| Baryum | 0,007 |
| Strontium | <0,001 |
| Gallium | 0,072 |
| Chromium | < 0,01 |
| Vanadium | 0,003 |

Table 4: SARIS-ICP-MS quantification results for an unused ceramic ring. Results are given for the backside in 1e15 atoms/cm²

Several rings are compared depending on the number of wafers ran prior to the optimized dry cleaning process (number 4) chosen thanks to the study as shown is paragraph 2. Graph 7 below compares typical tungsten values obtained for the different rings compared also to the post clean results, corresponding to graph 5. An accumulation of tungsten contamination is observed as a function of wafers ran. It means therefore that even the optimized cleaning process is not 100% efficient but undergoes a certain yield. If one take the hypothesis that cleaning process number 2 has an efficiency yield of 0%, it would indicate that cleaning process number 4 has at least a yield efficiency of 99,5%. The cumulative effect regarding tungsten contamination also indicates that sooner or later the ceramics parts are bound to be replaced, depending on the given cleaning process efficiency.




Graph 7: comparison between ceramics rings as a function of their lifetime and number of cleaning processes for tungsten contamination after peroxide extraction and ICP-MS analysis. Comparison also with the results obtained for the different cleaning processes as depicted in graph 5. Values are cumulative results of the four successive extractions for each ring and given in ng/g in logarithmic scale.

## Conclusion

A comparison between analytical techniques such as ICP-MS and particle counting associated to microscopic means allows to identify the suitable non destructive analytical protocol required to assess contamination level of alumina ceramics parts. The major contaminant found for such parts undergoing CVD process using $WF_6$ chemistry is obviously tungsten contamination. Among the wide panel of metals analyzed, this is the only one found as significantly sorting from the background noise. Even though this analytical protocol is not proven to be 100% efficient thanks to SARIS-ICP-MS data, it allows to select the most efficient industrial cleaning process regarding tungsten removal. The efficiency of the select process is demonstrated to be higher than 99,5% tungsten removal efficiency. Finally, this analytical procedure turns out as a valuable tool for predictive ceramics parts exchange which can be very useful for ceramics lifetime management for semiconductor industry.

## Acknowledgements:

LD would like to acknowledge Dr. Scott Anderson and Dr. Fuhe Li for their comments, suggestions and proofreading.
LD acknowledges ST Rousset, namely Hervé Dubus and Didier Bourdenet for their collaboration to the definition of design of experiment and ceramics samples supply.

## References:

1. "Retrait des particules: méthodes de nettoyage du silicium et évolution vers d'autres matériaux", F.Tardif, 8th Contaminexpert forum, march 11-13 2003.
2. "Cleaning solutions based on hydrogen peroxide for use in silicon Semiconductor industry", W.Kern and D.Puotinen, RCA review 31, p187, 1970
3. Wet cleaning in microelectronics in following book "Procédés de fabrication en micro-électronique", F.Tardif, Hermes Science Publications, 2003
4. F.H. Li and S. Anderson, Using Direct Solid Sampling ICP Mass Spectrometry to Complement SEM-EDX and SIMS in Characterizing Semiconductor Materials, in "Characterization and Metrology for ULSI Technology", Seiler D.G. et al. (Ed.), American Institute of Physics, New York, pp 715-719, 2003.