NICHIAS Technical Report
Volume 2 No.369 2015

〈Technical Report〉

Ensuring Cleanliness of Fluoropolymer products (Part 2 of 2)
- Measurement of TOC in trace amounts and metals in ultra-trace amounts in fluids in PFA tube transfer -

Masaaki Koubara from Tsurumi Laboratory, Research & Development Division
Minako Kaneko from Analysis Group, Research & Development Division

1. Introduction

As semiconductor devices are becoming miniaturized, there has been an increasing demand for higher levels of cleanliness for semiconductor manufacturing devices and for materials used for related facilities. Contamination of pure water or liquid chemicals in an order of magnitude of ppb (parts per billion) being used with semiconductor manufacturing equipment can prevent the manufacturing process from being started for weeks and even months. Even a slight contamination that can occur all of a sudden during a mass production run can impact production efficiency. To avoid these problems, it is important to minimize contamination of materials used for manufacturing facilities. Hence the need for measuring techniques that enable accurate monitoring of the occurrence and development of contamination.

Contaminants in semiconductor manufacturing processes can be roughly classified into particles, TOC in trace amounts and metals in ultra-trace amounts. As part of our study, accurate contaminants measuring techniques have been established and, using these methods, comparative evaluation was conducted on NICHIAS and competing-brand PFA tubes. Part 1 of our 2-part study, released in an earlier technical report, presented measuring techniques capable of minimizing erroneous particle counts caused by minute bubbles of air that enter the measuring and evaluation system. This report, Part 2 of our 2-part study, highlights techniques for minimizing contamination in measuring processes of trace TOC and ultra-trace metals.

2. Measurement of trace TOC

When we think about contaminants having serious impact on semiconductor manufacturing processes, the first thing that normally comes to our mind is particles, which is featured in Part 1 of our 2-part study. Equally important is TOC (Total Organic Carbon) which is used as a measure of fluid contamination by trace organic matter affecting manufacturing efficiency. While TOC in ultra-pure water is generally measured at POD (Point of Delivery) of the ultra-pure water production device, what affects the efficiency of semiconductor manufacturing processes is the water quality at the wafer-contacting point, or POP (Point of Process). This means that contamination should be minimized while ultra-pure water and liquid chemicals are being transferred from POD to POP. While NICHIAS has been offering tubing for semiconductor manufacturing and other devices, there has been a growing demand based on the anti-contamination requirement mentioned above for reduction in TOC from tubing and

related processed components.

To reduce TOC at POP, it is necessary to identify the source of TOC, which can be the tubing used or elsewhere, and take appropriate actions. However, that is not easy considering the sheer number of tubing components used and because TOC contamination is typically in an order of magnitude of ppb (parts per billion) (hereafter referred to as "trace TOC"), making it difficult to take accurate measurements on every single tubing component, let alone identifying the source. Ultra-pure water is most widely used for measuring trace TOC originating from tubing components. However, ultra-pure water can be easily degraded by impurities dissolving into it, making it unsuitable for trace TOC which requires highly precise measuring. In an attempt to overcome this, efforts were made to develop techniques that would enable accurate measuring of trace TOC.

2.1 Trace TOC measuring method

A number of TOC analyzers with different measuring principles and sensitivities are on the market. In our study, an ANATEL A-1000XP from Hach Ultra, the product that is capable of accurately analyzing trace TOC in ultra-pure water and that has been used for water quality control at leading semiconductor manufacturing companies, was used. After the analyzer's features including quantitative analysis accuracy were reconfirmed, measurements were taken on PFA tubes available on the market.

In measuring trace TOC, factors contributing to the degradation of measuring accuracy include changes with time after ultra-pure water samples are taken, inappropriate sample taking operation, contamination originating from the environment in which measurements are taken and the characteristics and conditions of the device being used for measurement. In our study, these factors were analyzed and measurements were taken of trace TOC in a highly accurate manner. Part of the results are discussed below.

It has been pointed out that, among factors contributing to the quality degradation of ultra-pure water, ambient contaminants play a significant role [1, 2]. This has been shared by NICHIAS analyses in that controlling the environment in which measurements are taken is extremely important. Simple experiments were conducted using beakers in an environment with a maximum ambient TOC concentration of 5 μg/m^3. Samples of ultra-pure water put in a beaker were measured for TOC concentration immediately after the samples were put into the beaker and 5 minutes later. It was found that the TOC concentration after 5 minutes was about 2 ppb higher than the initial concentration (**Figure 1**). Under the same test conditions, it was also found that TOC concentration was higher when samples were taken in conditions that allowed air bubbles to be generated than when the samples were taken in conditions that would not allow air bubble generation (**Figure 2**).

As discussed above, trace TOC measurement needs to be conducted in highly specified conditions including a controlled measuring environment, e.g. elimination of air bubbles.

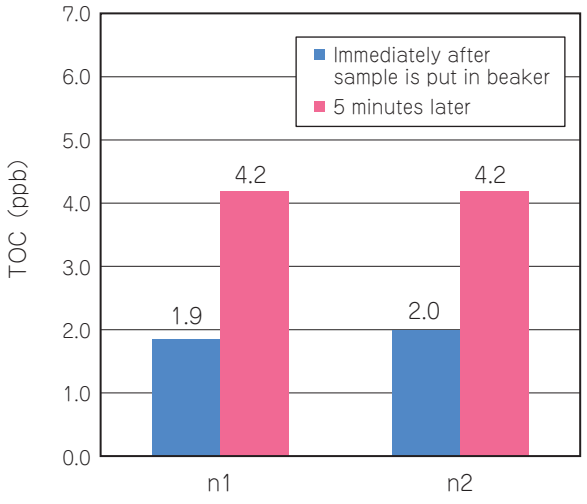

Figure 1. Change with time in TOC concentration

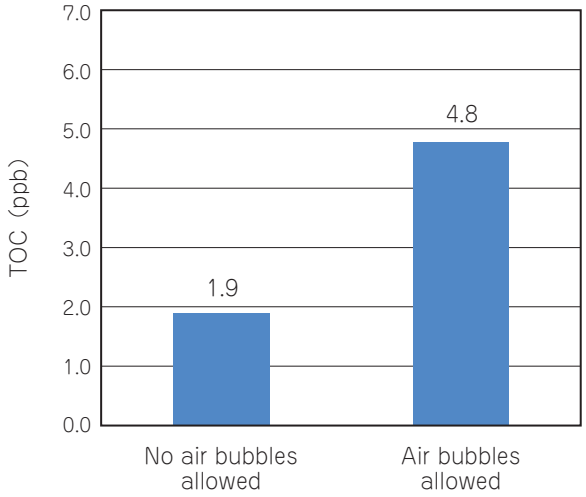

Figure 2. TOC concentration between different sample taking methods

2.2 Measurements

2.2.1 Blank measurement

Prior to measuring trace TOC originating from tubes, it was necessary to ensure that measured results would not be affected by external contaminants. For that, blank measurement was conducted. Blanks were measured by filling clean tubes with ultra-pure water, sealing the tubes and leaving them for 16 hours at room temperature in a static condition before measuring TOC concentration. As mentioned earlier, accuracy of trace TOC measurement can be easily affected by inappropriate sample taking operation. With that in mind, measurements were taken in an inert gas atmosphere, strictly following the specified procedures, to eliminate the possibility of external contamination. Through these efforts for optimum procedures and control of external influence, the blank measurement achieved a contamination level of about 2 ppb.

2.2.2 Measurement of marketed products for trace TOC

Using a method established through the efforts descried earlier, measurements for trace TOC were taken on NICHIAS TOMBO™ No.9003-PFA-HG "NAFLON™ PFA-HG tube" (hereafter referred to as the "PFA-HG") and competing-brand PFA tubes of similar dimensions (15.88 mm in inner diameter, 19.05 mm in outer diameter, 1 m in length). Prior to the measurement, 500 ml of water were passed through the tubes. (The tubes were fed with ultra-pure water and sealed. → The tubes were left in a static condition at room temperature for 16 hours.→ The tubes were measured for eluted TOC concentration.) The results showed that the PFA-HG had lower concentrations of eluted TOC than the competing-brand PFA tubes (**Figure 3**). In the next step, these tubes were measured using the same procedure to check for reduction in eluted TOC concentration. It was found that the eluted TOC concentration of the PFA-HG dropped to the level of the blank measurement. When using PFA tubes for devices used for manufacturing semiconductors and other products, the speed at which contamination levels drop directly affects restarting of the manufacturing facilities. Hence, the quicker the drop in eluted TOC concentration, the better. Again, the results of the trace TOC measurement showed that the PFA-HG had lower eluted TOC concentration and quicker drop in the concentration.

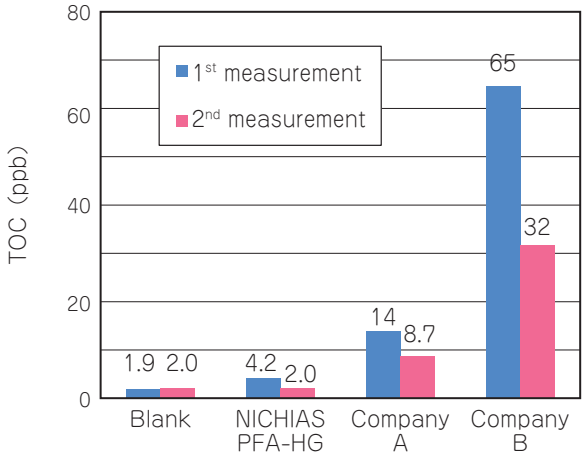

Figure 3. Measuring PFA tubes of different brands for TOC

2.3 Causes for TOC generation

There are a number of theories as to how TOC is generated. One of them is that thermal load on resin materials may play a role. PFA materials go through thermal processes including molding as well as secondary operations such as bending and welding. In these heating processes, resins go through thermal decomposition where TOC can be generated and stay inside the material. It is then thought that, depending on specific heating conditions, there can be difference in eluted TOC concentration (**Figure 4**).

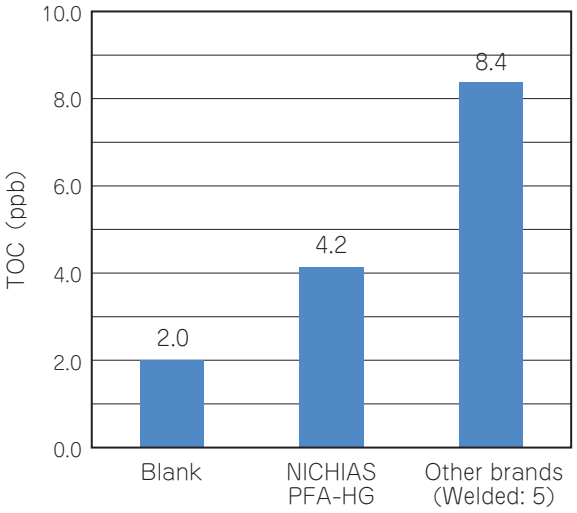

Figure 4. Welding and TOC concentration

3. Analysis for ultra-trace metals

Metal pollutants, even in trace amounts, can adversely impact the electrical properties of semiconductor devices. Because of that, there has been a high demand for elimination of metal pollutants. At NICHIAS, ICP-MS (Inductively Coupled Plasma Mass Spectrometry) has been used in highly sensitive and accurate analysis of metals on wafer surfaces and in the air for their contents and elution amounts.

In analyzing ultra-trace metals in an order of magnitude of ppt (parts per trillion), it is extremely important to not just ensure highest performance of the analyzers used but prevent contamination in pre-analysis preparation processes. As part of our study, fluoropolymer tubes were analyzed as described below for metal contaminants eluted from the tubes' inner surfaces.

3.1 Environment and facilities for analysis

NICHIAS operates a clean room of the ISO Class 1 (10 particles or less sized 0.1 μm and larger per cubic meter) and conducts pre-analysis treatment in a clean draft chamber and bench equipped with chemical filters. In our operations, ultra-pure water, reagents and analyzers are controlled for cleanliness. The ICP-MS at NICHIAS is an Agilent 7500S from Agilent Technologies.

3.2 Analysis methods used

Fluoropolymer tubes were cut using a ceramic knife, the cut tubes were filled with elution fluid, or a solution containing 3.6% hydrochloric acid, and the tubes' ends were closed. After the tubes were left at room temperature for 20 hours, the eluates were collected for measurement with the ICP-MS unit. Extreme care was taken when the solution was poured into the tubes to prevent any ingress of air and other contaminants. The equipment used was capable of analyzing tubes with inner diameters of 2 mm and greater. The tubes were cut into lengths that would produce a common inner tube area of 100 cm^2. As part of our analysis, the same elution procedures were repeated on the same tubes. The elements for analysis were selected according to SEMI F57-0312. For quantitative analysis, an analytical curve was produced based on the 3.6% hydrochloric acid concentration, and XSTC-22 from SPEX of the U.S. diluted to 1 - 1000 ppt was used as the standard solution.

3.3 Accuracy of the quantitative analysis

Pickled PFA-HG tubes (6.35 mm in inner di-

ameter, 9.52 mm in outer diameter, about 50 cm in length, about 100 cm^2 in inner surface area, about 16 g of elution fluid) were used as blanks. Elution was repeated three times on these same tubes (n=2). The results showed that all of the elements analyzed were below the quantitative lower limits (< 10 ppt, < 2 pg/cm^2), indicating that no contamination was introduced during the preparations for the analysis, or in other words, the analysis was conducted in a highly accurate manner.

3.4 Measurement of marketed PFA tubes for eluted metals

Analysis was conducted on PFA-HG tubes (6.35 mm in inner diameter, 9.52 mm in outer diameter, about 50 cm in length) and competing-brand PFA tubes with the same inner diameter for metal elution from the inner surfaces. For a 10-day period, elution was repeated four times and subsequent events were monitored (3 times on Day 1 + 7 days. Every elution was conducted with new fluid.). The results are shown in **Figure 5**. The total elution weights from the 1st elution (Day 1) were PFA-HG < Company B << Company A. From the 2nd elution onward, all of the elements including Cr eluted from the PFA-HG and Company A tubes were below the quantitative lower limits. On the other hand, Fe, Ni and other elements were detected from the Company B tubes. Contaminants attached on tube surfaces can be removed easily while those inside the tube are difficult to remove and tend to be detected over a long period of time. It points to the importance of controlling internal contaminants.

3.5 Measurement of contamination from secondary manufacturing operations

Tubes can be contaminated with metals during secondary manufacturing operations such as bending and welding. Welded tubes (15.88 mm in inner diameter, 19.05 mm in outer diameter, about 40 cm in length, about 200 cm^2 in inner surface area, about 80 g of elution fluid) were analyzed for metal elution from the inner surfaces. The results are shown in **Figure 6**. The total elution weight was 200 - 300 pg/cm^2,

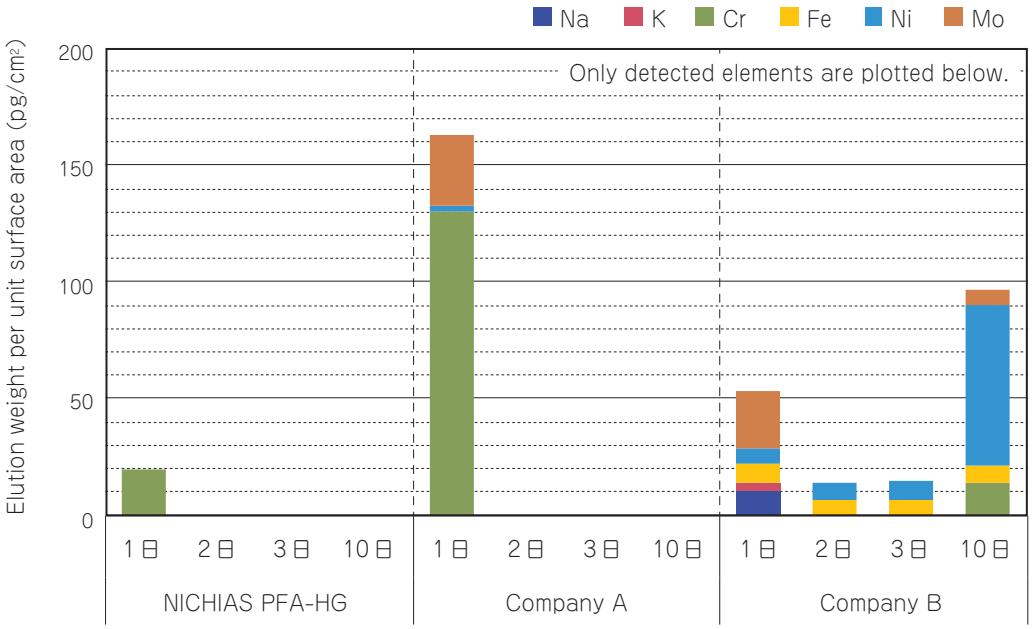

Figure 5. Metal elution from marketed PFA tubes

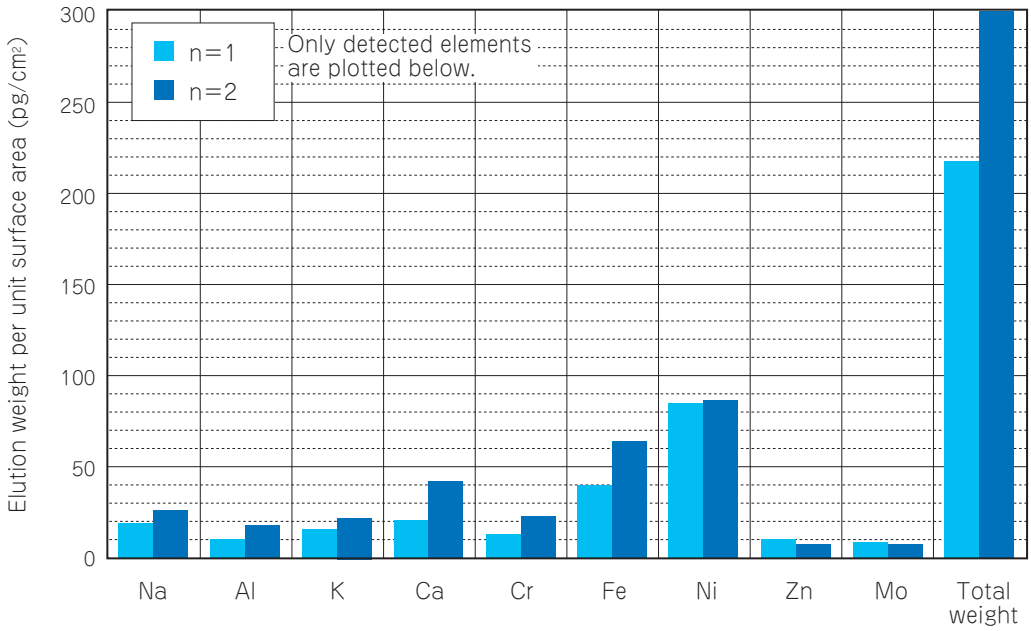

Figure 6. Metal elution from welded tubes

of which Fe and Ni were significant, clearly indicating contamination from secondary operations.

4. Conclusion

This report discusses efforts by NICHIAS to ensure cleanliness in manufacturing processes by eliminating major contaminants including particles, trace TOC and ultra-trace metals. To achieve accurate measurement of these trace contaminants, it is crucial to minimize the risk of contamination by shrinking air bubbles through pressurization (for particles), controlling the environment in which measurement takes place (for TOC) and strictly regulating pre-measurement preparation processes (for metals). It is anticipated that even more sophisticated anti-contamination techniques will need to be developed as demand for product cleanliness continues to grow.

To ensure product cleanliness, extreme care must be taken throughout the entire operation, from the selection of materials, controlling contamination in manufacturing facilities, establishing the proper manufacturing conditions, to product inspection, storage and transportation. To further advance the cleanliness of our tubes and other fluoropolymer products, we will continue our efforts in basic properties study and optimization of manufacturing method. The results of these efforts will certainly materialize in our future products.

<Acknowledgements>

As a manufacturer of materials, we have been receiving extensive support and cooperation from a range of partners in our research and development on advanced techniques for product cleanliness. On this opportunity, we especially would like to express our deepest appreciation to everyone at the New Industry Creation Hatchery Center of Tohoku University for their thorough guidance on the measurement of particles discussed in Part 1 of this report.

References

1) Yoshifumi Kuroki, Chromatography, 2012, 33, 75-83
2) Yoshifumi Kuroki, Analytical Chemistry, 2010, 59, No. 2, 85-93

* The measurements presented in this report should be used only as a guide and not as guaranteed values.
* This report is a modified version of the original article published in the November 2014 issue of the Clean Technology.

Authors

Masaaki Koubara
from Tsurumi Laboratory, Research & Development Division
Has been involved in the development of filters.
Currently engaged in study on technologies for ensuring product cleanliness.

Minako Kaneko
from Analysis Group, Research & Development Division
Has been involved in the development of analysis and evaluation techniques for product cleanliness.