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Ensuring Cleanliness of Fluoropolymer products (Part 1 of 2)

- Measurement of particles in fluids in PFA tube transfer -

Shun Ishikawa from Tsurumi Laboratory, Research & Development Division

1. Introduction

No other industry demands higher levels of cleanliness than the semiconductor industry, and the standard is being raised as semiconductors continue to evolve. To meet the rising standard, required cleanliness levels are being raised 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.

Contaminants can be roughly classified into particles (minute foreign particles), inorganic and organic contaminants and metal impurities. These substances can affect manufacturing processes physically or chemically, causing such problems as circuit pattern fault, haze generation and reduced reliability of gate elements. For these reasons, materials used for the manufacture of semiconductors must be kept clean and away from contaminants.

NICHIAS Corporation has been offering a range of fluoropolymer materials for semiconductor applications that are highly resistant to chemicals and heat. Among these materials, PFA and other types of tubing are used for transferring pure water and liquid chemicals and, as such, are considered to contribute greatly to the maintenance of ultra-cleanliness. For these reasons, it is extremely important to be able to monitor the occurrence and development of contamination. On the other hand, it is not easy to accurately measure contamination, typically minute and in trace amounts, with no external influence.

This report (consisting of 2 parts in total) discusses techniques for accurately measuring contaminants, minute and in trace amounts, with the 1st part relating to particles and the 2nd part to TOC in trace amounts and to metals in ultra-trace amounts. In addition, the results of research on contamination of NICHIAS and other PFA tubes in the field are presented in this report.

2. Measurement of particles

2.1 Problems with conventional measuring techniques

Two techniques are commonly for measuring particles in gases and liquids. One uses tools such as surface contamination detectors and electron microscopes with filters and wafers. The other uses particle counters with sensors that measure particles by detecting scattered laser beam caused by particles. The first technique enables grasping the shapes and compositions of particles via electron microscope images while the particles are being counted. The technique, however, is labor intensive, time consuming and costly. The second technique costs less than the first technique and is capable of automatically counting particles in fluids after they have gone through sensors. The technique is often used for counting particles originating from manufacturing line control and materials used. Liquid particle counters (hereafter referred to as "LPC") are used primarily for controlling ultra-pure water and for performance evaluation of liquid particle filters. However, LPCs have a problem that is not shared by gas particle counters. That is, bubbles which make it difficult to accurately measure particles in fluids. Specifically, when using a gas particle counter to measure particles in tubes, the tubes are connected to the counter in a clean room (hereafter referred to as "CR") and flow is adjusted to enable measurement. On the other hand, when using an LPC connected to tubes, and liquid transferred in a CR, measurement error (bubble noise) occurs, possibly caused by gases entering from the CR (through the tubes). Similarly, any dissolved air in fluids can be turned into tiny bubbles by vibration or pressure fluctuation, generating bubble noise.

This report presents a new technique that has been developed to accurately measure particles in liquids being transferred in tubes while minimizing the noise of bubbles of the air that has entered through the tubing or has dissolved in the liquid.

2.2 Solving problems

2.2.1 Particle measurement and evaluation system

Figure 1 shows the flow of the particle measurement and evaluation system used in our study. The system conforms to the "Particle Test Method Guide for Evaluation of Components Used in Ultrapure Water and Liquid Chemical Distribution Systems" (SEMI F104-0312) 1). The LPC used in the system was an HSLIS M65e of Spectris (Particle Measuring Systems), capable of measuring particles down to 0.065 μm in size. In order for the system to be able to accurately measure particles, fluids need to be run at a rate of 100 ml/min ±10%. Any excess fluids are diverted for drainage. The drainage channel is also used for purging air that enters the system during replacement of samples.

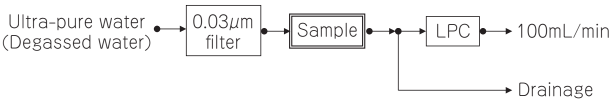

Figure 1. Flow of particle measurement and evaluation system

2.2.2 Bubble noise mitigation by pressurization

Experience tells us that bubble noise caused by air ingress, which is mentioned in 2.1, can be effectively mitigated by pressurizing the measurement and evaluation system and using degassed water 2). The following are the results of our trials on these methods.

It was thought that noise mitigation effects of pressurization and degassed water come from the following factors.

Factor 1: Soluble air volumes are increased by pressurization and degassed water.
Factor 2: Air bubbles are shrunk by pressurization.

Figure 2 shows a presumed relationship between pressure and soluble air volume based on Factor 1.

The solid line in **Figure 2** represents the solubility of air at 23℃, which was calculated based on the table of formulas and physical properties in the Chemical Engineering Handbook 6th Edition 3). With the system open to the atmospheric pressure, air can be dissolved in water up to a

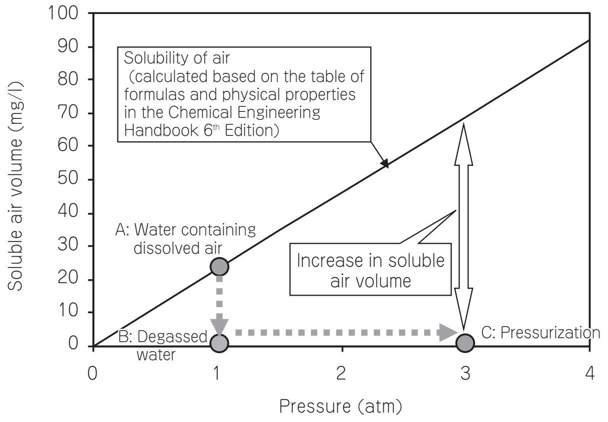

Figure 2. Presumed relationship between pressure and soluble air volume

soluble air volume of 23 m/l (A in **Figure 2**). In our study in which degassed water was used, the soluble air volume was considered to be 0 mg/l (B in **Figure 2**). Under these conditions, the ultra-pure water used was pressurized to 3 atm, which brought the soluble air volume to C, or 69 mg/l, in **Figure 2**. This shows that by using degassed water and pressurization, soluble air volume can be increased substantially, making air bubble removal easy.

The theory that air bubbles are shrunk by pressurization (Factor 2) is based on the Boyle's Law that the pressure on a gas and its volume are inversely proportional to each other. It was expected that pressurization shrinks the size of air bubbles in fluid, making them harder to be detected by an LPC.

To verify the above presumption, the following experiment was conducted. Clean PFA tubing (4 mm in inner diameter, 6 mm in outer diameter, 20 m in length) was connected to the sample unit of the measurement and evaluation system in **Figure 1** and, after confirming an agreement between the LPC's particle counts and noise levels, the PFA tubing was vibrated to let any dissolved air turn into bubbles. With this setup, average particle counts were obtained for a duration of 15 minutes, from the start of vibration until 5 minutes after the end of vibration, at various pressure and flow rate settings. The results are shown in **Figure 3**. By maintaining the pressure in the measurement and evaluation system at 2 atm, air bubble noise was effectively suppressed at any of the four flow rates used.

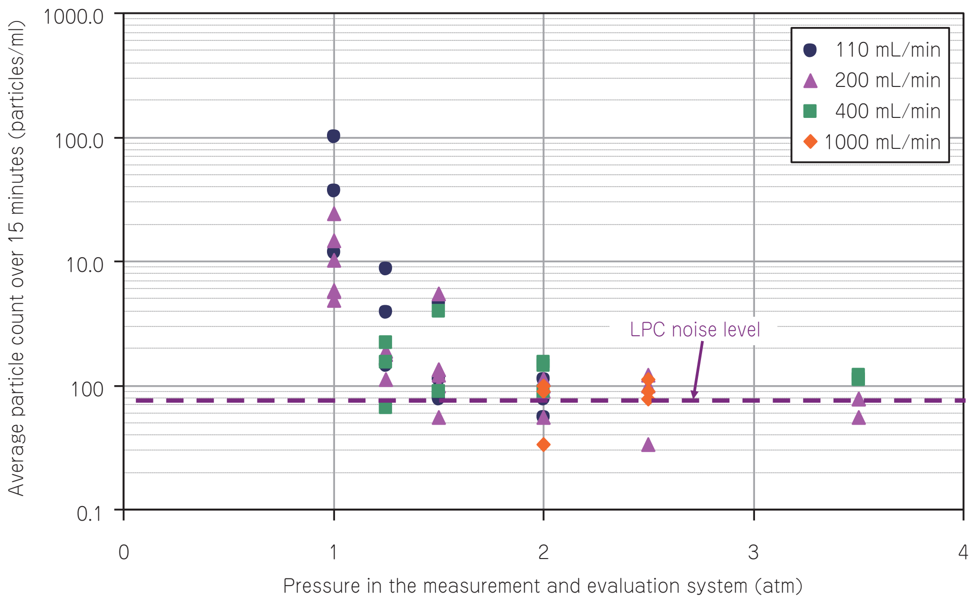

Figure 3. Effect of system pressure on air bubble noise

2.3 Comparative measurements

Using the air bubble removal through pressurization method described in 2.2, comparative measurements were conducted on NICHIAS TOMBO™ No.9003-PFA-HG "NAFLON™ PFA-HG tube" (hereafter referred to as the "PFA-HG") and competing PFA tubes of similar dimensions (4.35 mm in inner diameter, 6.35 mm in outer diameter, 20 m in length). Measurements were taken in accordance with SEMI F104-0312 using a system pressure of 3 atm, a flow rate of 150 ml/min to the sample unit, a flow rate of 100 ml/min to the LPC and an excess flow drain rate of 50 ml/min. Clean tubes were used to grasp the significance of errors in particle counts attributable to sample replacement. The results are shown in **Figure 4**. The X axis represents flow rate while the Y axis represents particle count. Logarithmic graphs cannot show "no particle per milliliter" results, which therefore were blotted as "1 particle per milliliter" for expedience.

Particle counts while using clean tubes converged several minutes after sample replacement. Using these counts as blanks, particle counts of the competing-brand PFA tubes were examined. The results show different contamination levels of different tubes and they all are nonetheless marketed as PFA tubes. With the above, it can be said that a particle counting method has been established.

The 2nd part of this report will discuss measuring methods for TOC in trace amounts and metals in ultra-trace amounts as well as the results of particle counts on competing-brand PFA tubes.

References

1) SEMI (2012) "Particle Test Method Guide for Evaluation of Components Used in Ultrapure Water and Liquid Chemical Distribution Systems" SEMI F104-0312
2) Kazuo Ichijo (2002) "Particulate Measurement in HDD Applications" IDEMA Japan News No. 57 p4
3) The Society of Chemical Engineers, Japan (1999) "Chemical Engineering Handbook" (Maruzen)

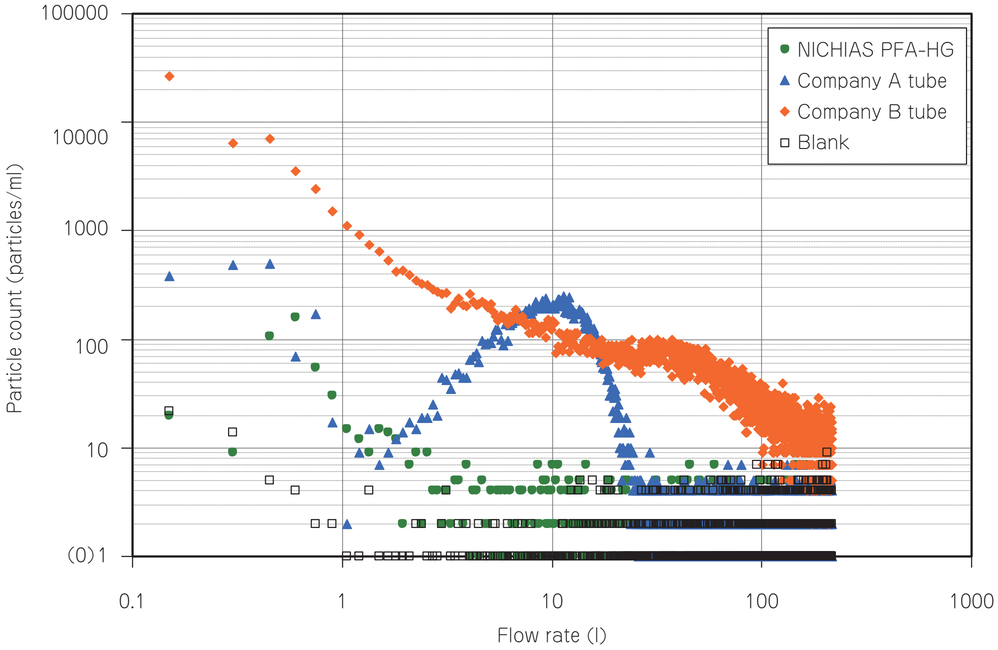

Figure 4. PFA tubes from different brands and generated particles

* "TOMBO" is a registered trade mark or a trade mark of NICHIAS Corporation.
* "NAFLON" is a trade mark of NICHIAS Corporation.
* The measurements presented in this report should be used only as a guide and not as guaranteed values.
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Author

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