Next-Generation Nanoporous PTFE Membrane

Hirokazu KATAYAMA*, Fumihiro HAYASHI, Naoki SHIMBARA, Atsushi UNO,
Yoshimasa SUZUKI and Yasuhiro OKUDA

Porous polytetrafluoroethylene (PTFE) was invented by Sumitomo Electric Industries, Ltd. using its stretching technology, and has been widely used for POREFLON microfiltration membrane or other products. Porous PTFE filters are particularly advantageous for the filtration of chemicals such as strong acid or alkali and, therefore, commonly used in the manufacturing process of semiconductor wafers, flat panel displays, and other electronic components. To enhance the cleanliness, PTFE membranes need to have smaller pores. This paper describes our new technology for generating nano-sized pores, alternative to the conventional stretching technology, and the resultant nanoporous PTFE membrane.

Keywords: porous membrane, filter, fluororesin, micropore, liquid filtration

1. Introduction

Sumitomo Electric Industries, Ltd. invented a technique to make polytetrafluoroethylene (PTFE) porous using PTFE stretching technology, which was patented in 1962.(1) Drawing on the technique, the company has subsequently released various porous PTFE products such as filters and hollow fiber products under the trade name of POREFLON. Porous PTFE filters, one of these porous PTFE products, use sheet-type porous PTFE membranes that have numerous micropores with a diameter of 10 µm or less. Taking advantage of their excellent chemical resistance, they have been used as microfiltration membranes in obtaining high-purity chemical solutions in the manufacturing processes of semiconductors, liquid crystal panels, and other electronic components. Porous PTFE membranes are also used to produce electrical wire insulating material due to their low dielectric properties and are used as gas permeable and waterproof films for automobiles and electronic components due to their excellent water repellency and gas permeability. Water treatment membrane modules, a porous PTFE hollow fiber product, are used for treatment of industrial wastewater and water treatment in food industries.(2)

A porous PTFE membrane filter that has excellent chemical resistance, heat resistance, and non-elution properties is an essential component for the filtration of acidic or alkaline chemical solutions used in the manufacturing processes of semiconductor wafers, liquid crystal panels, and other electronic components. In the semiconductor industry, in particular, the development of higher density chips and wafers with a larger diameter increases the necessity of obtaining higher-purity chemical solutions to clean wafers. The need for porous PTFE membrane filters, which can remove minute foreign substances, has been increasing. We have developed a new technology that can replace the conventional stretching technology to create nanoporous PTFE membranes. This paper describes this unique technology for generating pores with a diameter of less than 50 nm, which cannot be generated by conventional technology.

2. Technology Trends and Development Goals for Liquid Filtration Membranes in Semiconductor Manufacturing

As shown in Fig. 1, hydrogen fluoride solution, ammonia and hydrogen peroxide, and hydrochloric acid and hydrogen peroxide are used as washing agents in the removal process of a silicon oxide layer on the surface of wafers, the removal process of organic particles, and the removal process of metal particles, respectively, to clean silicon wafers in semiconductor manufacturing.(3) To reduce the volume of waste fluid, foreign substances in the chemical solutions are filtered after the cleaning process and the solutions are recycled. As filters must be resistant to acidic, alkaline or heated chemical solutions used for cleaning, and must prevent the elution of the components to solutions, porous PTFE membranes, which satisfy these requirements, are used as filters.

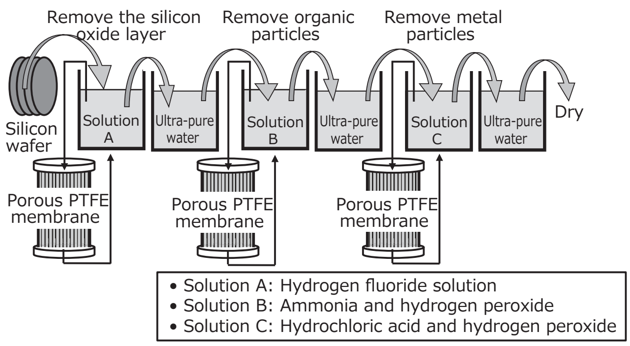


Fig. 1. Silicon wafer cleaning process in semiconductor manufacturing

In the semiconductor industry, manufacturing of higher density and faster IC chips (microfabrication) increases the necessity of obtaining higher-purity chemical solutions to clean wafers. To remove minute foreign substances, porous PTFE membranes that have pores with a diameter of less than 50 nm are required. Based on these technology trends, we set up the following development goals: the mean flow pore size*[1] to be 50 nm or less and the isopropyl alcohol (IPA) flow rate*[2] and mechanical strength to be equivalent to those of conventional porous PTFE membranes, as indicated in Table 1.

Table 1. Development goals of liquid filtration membrane in semiconductor manufacturing

Item			Unit	Measurement method	Goal
Pore size	Mean flow pore size		nm	ASTM F-316	≤50
	Diameter: 30 nm Polystyrene latex (PSL) collection efficiency		%	Measure the changes in concentration of 200 ppm PSL solution with 30 nm particles before and after filtration using a spectrophotometer	≥50
Flow	IPA flow rate		ml/min/cm^2/100kPa	JIS P 8117	≥0.8
	Air flow rate		ml/min/cm^2/1.2kPa	JIS P 8117	≥25
Mechanical strength	Thickness		µm	Dial gauge	≤100
	Tensile strength	Machine Direction (MD)	MPa	JIS K 7127	≥5
		Transverse Direction (TD)	MPa	JIS K 7127	≥5

3. Development of New Porous PTFE Membrane Filters

3-1 Designing a new filter structure

Regarding the relationship between the mean flow pore size and IPA flow rate of a conventional porous PTFE membrane, the flow rate decreases as the pore size decreases. To obtain a flow rate equivalent to that of a conventional porous PTFE membrane from a new membrane that has pores with a diameter of 50 nm or less, it must have an equivalent porosity*[3] and a thickness of 2 µm or less. In addition, to obtain the mechanical strength necessary for practical filter applications, we employed a double-layer structure comprising a filter layer, which has a pore size of 50 nm or less and a membrane thickness of 2 µm or less, and a support layer, which has been used for field-proven conventional porous PTFE membranes (membrane thickness: 30-100 µm) (Fig. 2).

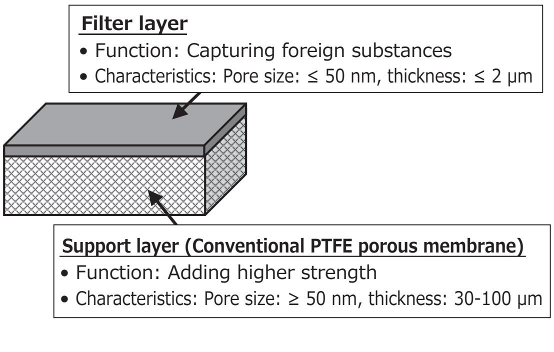


Fig. 2. Structure of the new porous PTFE membrane filter

3-2 Developing the filter layer

The production method for conventional porous PTFE membranes is shown in Fig. 3. PTFE fine powder produced by emulsion polymerization is mixed with extrusion lubricant. Through the extrusion molding, rolling, and stretching processes, PTFE becomes microporous.[(4),(5)] The conventional production method does not generate micropores with a diameter of 50 nm or less because a rolled PTFE substance has voids of 50 nm or more between particles before the process of making micropores. Therefore, we explored (1) original material and technology for generating numerous nano-sized pores in nonporous PTFE, (2) a thinner filter layer, and (3) multilayering technology for the filter layer and support layer.

To develop new technology for generating nano-sized pores, we looked at the raw materials of PTFE, membrane formation, nonporous membrane post-processing technology, and a new technology for opening up pores. As a result, we successfully developed a new nano-sized pore fabrication technology that allows us to control the mean flow pore size in a range from 4 to 50 nm.

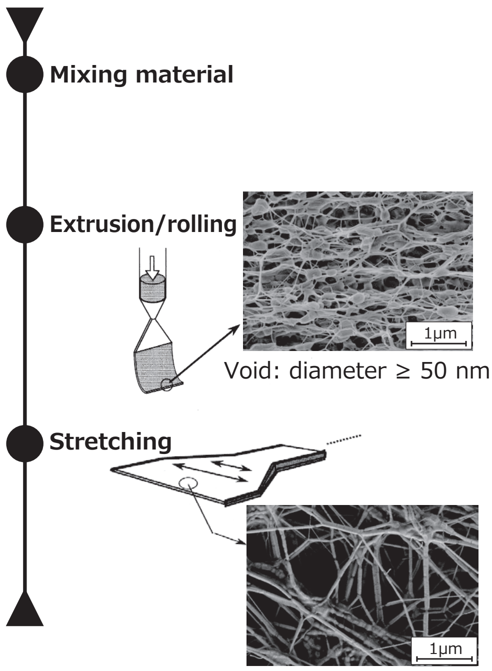


Fig. 3. Production method for conventional membranes utilizing stretching technology

Figure 4 shows the results of measuring the collection efficiency*[4] of polystyrene latex (PSL) with pores of 30 nm in diameter. With the new porous PTFE membrane, a smaller diameter means higher collection efficiency. Our new membrane has a mean flow pore size of 50 nm or less, resulting in a collection efficiency much higher than the development goal of 50%.

As shown in Fig. 5, the new porous PTFE membrane with a mean flow pore size of 35 nm achieves an IPA flow rate equivalent to that of conventional membranes.

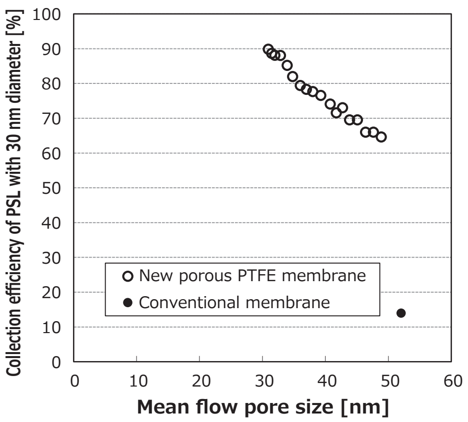


Fig. 4. Mean flow pore size and 30 nm PSL collection efficiency of the new porous PTFE membrane and a conventional membrane

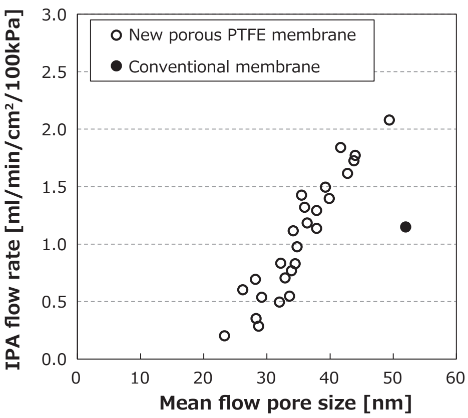


Fig. 5. Mean flow pore size and IPA flow rate of the new PTFE porous membrane and a conventional membrane

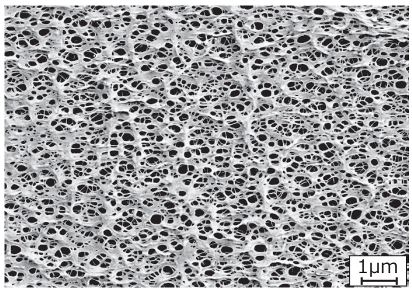
3-3 Characteristics of the new porous PTFE membrane filter

Based on the above-mentioned new porous PTFE technology, a mean flow pore size of a filter to satisfy the development goals was determined as 35 nm. Table 2 shows the characteristics of the new porous PTFE membrane filter experimentally produced by the technology. The new membrane achieved a practical-level IPA flow rate as a liquid filtration membrane, which cannot be achieved by conventional membranes produced by stretching technology. The collection efficiency of PSL with pores of 30 nm in diameter was much higher than the development goal of 50%. Also, the mechanical strength was equivalent to or better than that of conventional membranes and the development goals were accordingly achieved.

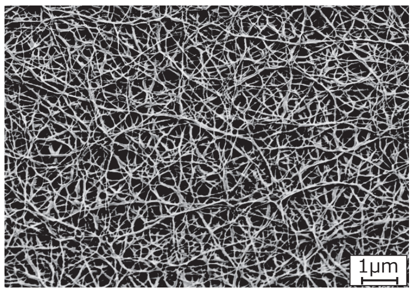
Figure 6 shows scanning electron microscope (SEM) images of the filter layer of the new porous PTFE membrane. It is noticeable that more minute pores have been generated with higher density than for the conventional membrane and the shape of the pores is different from the conventional shape. Perforated area ratios estimated by processing the SEM images are 31% for the new porous PTFE membrane filter and 33% for the conventional membrane. Although the thickness of the filter layer is too thin (2 μm) to measure the porosity, the porosity of the new membrane is considered to be equivalent to that of conventional membranes in consideration of these perforated area ratios.

Table 2. Characteristics of the new porous PTFE membrane filter

Item			Unit	Goal	Characteristics
Pore size	Mean flow pore size		nm	≤50	35
	Diameter: 30 nm Polystyrene latex (PSL) collection efficiency		%	≥50	80
Flow	IPA flow rate		ml/min/ cm^2/100kPa	≥0.8	1.3
	Air flow rate		ml/min/ cm^2/100kPa	≥25	30
Mechanical strength	Thickness		μm	≤100	50
	Tensile strength	Machine Drection (MD)	MPa	≥5	29
		Transverse Direction (TD)	MPa	≥5	13



New porous PTFE membrane filter



Conventional membrane

Fig. 6. SEM images of the new porous PTFE membrane and a conventional membrane (surfaces)

The cross-sectional SEM images shown in Fig. 7 reveal that a filter layer with a thickness of 1 μm is formed on the support layer and that more minute pores are distributed along the vertical direction in the filter layer than is the case for the conventional membrane.

We have also established a production technology for new porous PTFE membrane filters with a width of 200 mm or more and a length of 15 m or more.

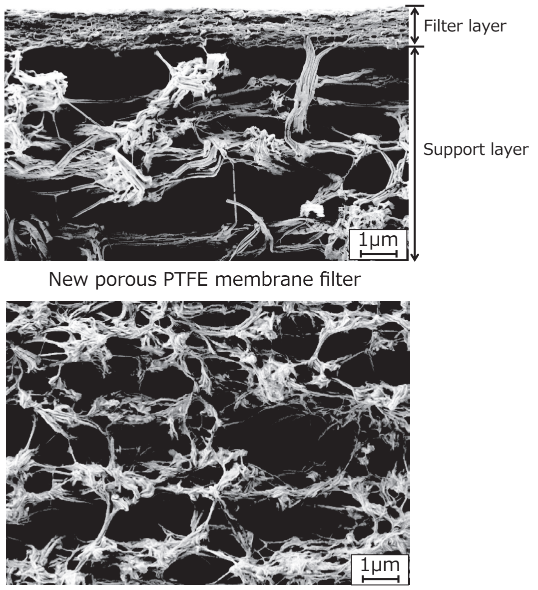


Fig. 7. SEM images of the new porous PTFE membrane and a conventional membrane (cross section)

4. Conclusion

As IC chip technology trends in the semiconductor industry are moving towards a finer pitch, the need for porous membranes with smaller pores for filtering chemical solutions have been increasing. We have developed a new porous PTFE technology that generates nanopores with a diameter of 50 nm or less, which cannot be achieved by conventional porous PTFE technology. This technology enables us to produce a porous PTFE membrane filter with a double-layer structure. The structure comprises a filter layer, which is 2 µm or less in thickness and has pores of 4-50 nm in diameter, and a support layer, which is 30-100 µm in thickness and has pores of 50 nm or larger in diameter. The filter will find wide applications including water treatment and food processing, as well as the filtration of chemical solutions in semiconductor manufacturing (Fig. 8).[6]

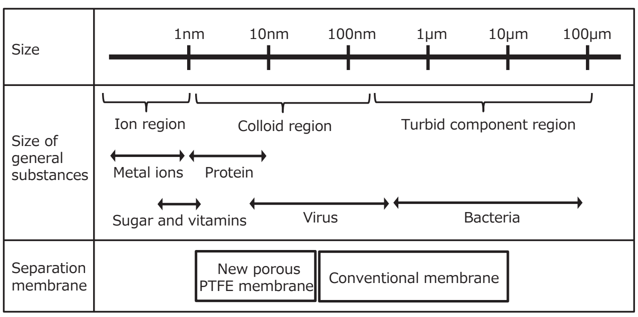


Fig. 8. Applications for the new porous PTFE membrane and conventional membranes

• POREFLON is a trademark or registered trademark of Sumitomo Electric Industries, Ltd.

Technical Terms

∗1 Mean flow pore size: The mean flow pore size is calculated by the pore size distribution measurement method using the bubble point method. By applying air pressure from one side of a membrane whose pores are filled with liquid with low surface tension, the relationship between the differential pressure and the flow rate is measured. The wet curve is measured after impregnating the sample and the dry curve is measured in a dry state. The mean flow pore size is the pore size calculated at a differential pressure where the wet curve crosses the half-dry curve that is calculated by dividing the flow of the dry curve by two.[7]

∗2 Flow rate: An indicator that shows the filtration performance of a porous membrane, using the volume of isopropyl alcohol and air that passes through the membrane.

∗3 Porosity: The ratio of the pore volume to the total volume of a membrane.

∗4 Collection efficiency: The value calculated from the ratio of concentrations of spherical PSL particles before and after passing through a filter membrane.

References

(1) Japanese Examined Patent Application Publication No.42-13560
(2) Sumitomo Electoric Industories, Ltd. Website http://www.sei.co.jp/poreflon/about/, http://www.sei-sfp.co.jp/products/poreflon-membrane.html
(3) T. Omi et al., “Kinzokuosen no Kyuchaku•Ridatsu-Kikou,” Wet Science ga Hiraku Product Innovation, pp. 25-40 (2001)
(4) M. Tanigaki et al., “Structure control and function of PTFE membranes by stretching method,” MEMBRANE, vol.26, no.3, pp.141-147 (2001)
(5) T. Satogawa et al., “Fusso-Jyushi Handbook,” pp.29-32, nikkankougyou shinbun (1990)
(6) Y. Takeuchi et al., “Takoushitsutai no Seishitsu to sono ouyougijyutsu,” pp.792-793, Fuji•techno-System, Ltd. (1999)
(7) Gifu-ken Sangyougijyutsu center kami kenkyubu, “San Gi Se news,” Gifu-ken Sangyougijyutsu center (July 2009)

Contributors The lead author is indicated by an asterisk (*).

H. KATAYAMA*

• Energy and Electronics Materials Laboratory

F. HAYASHI

• Assistant General Manager, Sumitomo Electric Fine Polymer, Inc.

N. SHIMBARA

• Ph.D.
Senior Assistant Manager, Energy and Electronics Materials Laboratory

A. UNO

• Senior Assistant Manager, Sumitomo Electric Fine Polymer, Inc.

Y. SUZUKI

• Manager, Sumitomo Electric Fine Polymer, Inc.

Y. OKUDA

• Ph.D.
Manager, Energy and Electronics Materials Laboratory