Application of Polyimide Porous Membrane to Photopolymer Filter

Tsukasa Sugawara¹*, Isao Hirano², Kensuke Kobayashi³, and Akira Kawai⁴

¹ PF Business Promotion Division, Tokyo Ohka Kogyo Corporate Limited, 1590 Tabata, Samukawa-machi, Koza-gun, Kanagawa 253-0114, Japan
² New Business Development Division, Tokyo Ohka Kogyo Corporate Limited, 1590 Tabata, Samukawa-machi, Koza-gun, Kanagawa 253-0114, Japan
³ Inspection Section, Gotemba Plant, Tokyo Ohka Kogyo Corporate Limited, 1-1 Komakado, Gotemba-shi, Shizuoka 412-0038, Japan
⁴ Department of Electrical Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan
*tsukasa-sugawara@tok.co.jp

Application of a polyimide porous membrane having a three dimensional homogeneous structure to a photopolymer filter for semiconductors was examined. When polymer solution was passed through the polyimide porous membrane, there was no change in the molecular weight of the nonpolar polystyrene, but the high molecular weight molecules of the polar ArF model photopolymer T001 were selectively removed. Smaller pores and greater specific surface area in the polyimide porous membrane improve the adsorption efficiency, and the high molecular weight polar polymer removal property was promoted. Filtering photopolymers with the polyimide porous membrane suppressed the increase in defects that occurs with aging.

Keywords: Polyimide, Filtration, Photopolymer, Porous membrane

1. Introduction

It is very important to reduce the defects and improve the yield in leading-edge semiconductor manufacturing processes [1-3]. For the reduction of defects, removal of the contamination source by filtration is effective, and filter makers are working to improve the filtering performance by decreasing the pore size and imparting adsorption property to the membrane [4,5].

Filters for semiconductors are required to have chemical resistance and cleanliness [6]. We focused on polyimide which has high purity and excellent chemical resistance as a filter membrane for semiconductors. In our previous paper, we reported on polyimide porous membranes with fine pores and high specific surface area prepared by dispersing micro silica in polyamic acid and removing silica after imidization [7].

In this paper, application of a polyimide porous membrane to a filter of photopolymers for semiconductors was investigated. First, nonpolar polystyrene and high polarity model polymer were filtered through a porous polyimide membrane and the filtration effect was evaluated. Next, the influence of the pore diameter and the specific surface area of the porous polyimide membrane on the filtration was investigated. Finally, the polymer solution after filtration was aged, and the change in the amount of defects on a wafer was confirmed.

2. Experimental

2.1. Materials

Table 1 shows the structure and molecular weight of polymers used in this paper.

The nonpolar polystyrene EASICAL PS-1 (Agilent Technologies, Inc.) was adjusted to 50 ppm with propyleneglycol monomethyl ether acetate (PGMEA).

The ArF high-polarity model photopolymer T001 was prepared by free radical solution
Table 1. Polymer structure and molecular weight.

| Polymer        | Structure | Molecular Weight |
|----------------|-----------|------------------|
| polystyrene    | ![Structure](image) | $M_w: 7,000,000$/$840,000$ $140,000/30,000/3,000$ |
| T001           | ![Structure](image) | $M_w: 1,200,000$/$660,000/10,000$ |

Polymerization of the monomers 2-ethyl-2-cyclohexyl methacrylate (ECHMA), $\gamma$-butyrolactone methacrylate (GBLMA) and 1-hydroxy-3-adamantyl methacrylate (HadMA) [8]. For example, T001 of $M_w$ 10,000 was prepared by the following procedure. 6.048 g of GBLMA, 4.704 g of ECHMA and 4.880 g of HAdMA were mixed in a flask with 25 mL of PGMEA. 0.786 g of dimethyl 2,2'-azobis(2-methylpropionate) was added as a radical initiator, and the mixture was stirred at 348 K for 4 hours under a dry nitrogen flow. The mixture was precipitated in 1 L of methanol and the precipitated polymer was filtered through a ceramic filter and thoroughly washed with methanol. The polymer was dried in a vacuum oven at 60 °C overnight. Similarly, polymerization to a $M_w$ of 660,000 was carried out by stirring with 0.958 mg of a radical initiator for 10 hours and polymerization to a $M_w$ of 1,200,000 was carried out by stirring for 20 hours using 0.479 mg of a radical initiator. NMR (AVANCE-600, Bruker Co.) revealed that the monomer unit ratio of these polymers is $x = 35$, $y = 40$, and $z = 25$ in Table 1. Their molecular weights were determined by GPC (LC-VP, Shimadzu Corporation) using a polystyrene standard. Each polymer was adjusted to 50 ppm with PGMEA.

2.2. Filtration

Figure 1 shows the filtering equipment. Filtration was carried out by laminating two polyimide porous membranes of 40 mm in diameter using a glass filter holder. The filtrate volume was 25 mL. The polymer solution was passed through a polyimide porous membrane by reducing the pressure to 800 hPa with a vacuum pump. The polymer solution after filtration was dried under a dry nitrogen flow overnight, the dried polymer was dissolved with 2 mL of tetrahydrofuran, and the molecular weight was measured by GPC. 2.5 mL of the polymer solution was applied to a silicon wafer at 1500 rpm using LITHIUS Pro-Z (Tokyo Electron Ltd.), and the polymer on the wafer was dried at 120 °C for 1 minute. After drying, defects of 50 nm or more on the polymer surface were counted with SP5XP (KLA-Tencor Corporation). Thus, the influence of filtration on aging was confirmed.

3. Results and discussion

3.1. Polarity and molecular weight

To begin with, the GPC results of polystyrene solution, which is a low polarity polymer, before and after filtration with polyimide filter are shown in Fig. 2. There was no change in molecular weight after filtration, showing that polystyrene with low polarity was not filtered out by the polyimide film when the molecular weight was 7,000,000 or less. The GPC results before and after filtration of the polar polymer T001 are shown in Fig. 3. The graph shows that polymers...
3.2. Pore size and specific surface area

In order to clarify the adsorption mechanism of the porous polyimide membrane, the filtration test of T001 was carried out with three types of membranes having the same porosity and film thickness but different pore size. As in our previous report, membranes with different pore sizes were prepared by dispersing silica fine particles in polyamic acid and removing silica after imidization [7]. Porous membranes were fabricated with silica whose diameters were 100 nm, 300 nm, and 2500 nm. Figure 4 is a SEM photograph of each membrane surface. As shown in Fig. 5, it was found that the smaller the pore diameter, the higher molecular weight polymers were removed.

In order to clarify the reason why the removal efficiency improves as the pore size decreases, a filtration test was performed with two membranes with silica diameter of 100 nm and 300 nm but the same specific surface area. The specific surface area of the spherical silica can be calculated with Eq. (1). Here, $S_m$ is the specific surface area per unit mass, $\rho$ is the density, and $D$ is the diameter.

$$S_m = \frac{6}{\rho D} \quad (1)$$

Since the specific surface area of the porous membrane depends on the specific surface area of the silica fine particles, six membranes with a pore size of 300 nm and two membranes with a pore size of 100 nm are considered to have substantially the same specific surface area. Therefore, the filtration test of T001 was carried out with a filter obtained by stacking six membranes with a pore diameter of 300 nm and a filter with two membranes with a pore diameter of 100 nm, and the change in molecular weight after the filtration was compared by GPC. Figure 6 shows that the membrane with a pore diameter of 100 nm removes more high molecular weight polymers than the membrane with a pore size of 300 nm. The reason for this may be that the opportunities for adsorption are numerous in a membrane having a small pore diameter because...
the distance between the high molecular weight polymer and the membrane surface is small [11].

3.3. Aging test

Finally, the effect of porous polyimide removal of high molecular weight polymers in T001 was confirmed by an aging test. T001 filtered with a polyimide filter and unfiltered T001 were aged at 40 °C for 1 week, each was coated on a silicon wafer, and defects of 50 nm or more were counted with SP5X. Figure 7 is the defect map. The number of defects before the aging test of T001 was 190. Defects of the unfiltered polymer solution increased to 1522 after aging. On the other hand, the number of defects in T001 that was aged after filtration was 171, showing that increase in defects over time was suppressed. We believe that this is a result of removal of high molecular weight molecules by filtration, which prevents further polymerization and gelling of these molecules due to aging [12-14].

![Defect map of T001](image)

Fig. 7. Defect map of T001.

4. Conclusion

We evaluated the application of polyimide porous membrane to filters for semiconductors. When a high polarity polymer solution was passed through the polyimide porous membrane, the amount of high molecular weight polymer was reduced due to adsorption, but the molecular weight of a low polarity polymer solution was not changed. Among polyimide porous membranes whose porosity is the same, a membrane having a smaller pore size is superior in removal efficiency of polymers with high polarity and high molecular weight. It was revealed that when a highly polar and high molecular weight polymer solution was filtered with a polyimide porous membrane, it was possible to suppress the increase in defects that occurs with aging.

References
1. T. Umeda, S. Tsuzuki, T. Takakura, and M. Tadokoro, J. Photopolym. Sci. Technol., 28 (2015) 653.
2. B. Gotlinsky, M. Mesawich, and D. Hall, Proc. Arch Interface Conf., (2003).
3. T. H. Ko, K. H. Lo, C. H. Wu, C. Yu. Chang, C. J. Lee, and J. Lin, J. Photopolym. Sci. Technol., 29 (2016) 793.
4. M. Ulbricht, Polymer, 47 (2006) 2217.
5. T. Umeda, S. Tsuzuki, and T. Numaguchi, Proc. SPIE, 7273 (2009) 72734B.
6. R. Varanasi, T. Umeda, M. Mesawich, P. Connor, and L. Johnson, J. Photopolym. Sci. Technol., 30 (2017) 639.
7. T. Sugawara, J. Koshiyama, and A. Kawai, J. Photopolym. Sci. Technol., 31 (2018) 437.
8. K. Nozaki and E. Yano, J. Photopolym. Sci. Technol., 10 (1997) 545.
9. T. Kohyama, Proc. SPIE, 8325 (2012) 83252I.
10. T. Umeda, T. Matsumiya, H. Yamano, and S. Tsuzuki, J. Photopolym. Sci. Technol., 29 (2016) 675.
11. I. Abe, J. Oleo Sci., 2 (2002) 275 (in Japanese).
12. P. R. Delgadillo, R. Harukawa, M. Suri, S. Durant, A. Cross, V. R. Nagaswami, D. V. D. Heuvel, R. Gronheid, and P. Nealey, Proc. SPIE, 8680 (2013) 86800L.
13. T. Hagiwara, K. Saito, H. Chaki, S. Matsuo, M. Inoue, S. Muranaka, Y. Ota, and M. Matsuura, J. Photopolym. Sci. Technol., 28 (2015) 17.
14. Y. Wei, S. Brandl, and F. Goodwin, Proc. SPIE, 6923 (2008) 69231Y.