In-Situ Observation of Permeation Behavior and Structural Analysis of Polyimide Membrane with Electrical Properties

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An ethanol aqueous solution was made to permeate into a polyimide membrane of three-dimensional porous structure, and the permeation behavior of the solution and the structure of the membrane were determined in situ based on the electrical characteristics. The experiment was carried out with a polyimide porous membrane having a porosity of 70%. The permeation rate of the solution into the membrane was calculated from the relationship between the time after drops of the ethanol aqueous solution began to be applied and the electrostatic capacitance. As a result, it was found that the solution quickly permeated into the porous membrane after drops began to be applied and then gradually filled the whole membrane. Similarly, the measured permeability of the surface of the polyimide porous membrane facing the air and the surface facing the substrate and SEM observation showed that the air-facing surface had a large opening area so that a solution easily permeates. As the rings of the imide group progressively opened due to alkali treatment, the relaxation time of the porous membrane became longer.

Keywords: Polyimide, Electrical property, Membrane, Capacitance, Permeation

1. Introduction

In semiconductor device manufacturing processes, removal of particles in the photoresist by filtration is required to improve device performance and production yield and reduce cost. Porous polyimide is clean and excellent in heat resistance and chemical resistance, so it is suitable for semiconductor filter membrane. In the previous paper, we reported on a process for fabrication a polyimide porous membrane with a pore size of nano order suitable for semiconductor filter membranes [1].

In evaluating the performance of a filter membrane, it is important to elucidate its permeability to solutions and its electrical characteristics [2-5]. Electrical properties are often measured in the structural evaluation of ceramics, inorganic materials and composites [6-9], and they also are useful in structural evaluation of organic materials [10-12]. The dielectric constant and dielectric relaxation are highly sensitive to and accurately reflect differences in the state of materials, so they are suited for in situ observation and structural analysis inside the membrane [13-15]. This suggests the possibility of monitoring the state of the filter by monitoring its dielectric properties.

In this paper, the electric properties were measured by applying an ethanol aqueous solution dropwise onto a polyimide membrane with three-dimensionally homogeneous porous structure sandwiched between electrodes. First, the electrostatic capacitance of a polyimide porous membrane with a porosity of 70% and a film thickness of 40 μm was measured. Then, the permeability of an ethanol aqueous solution into the porous membrane was calculated from the change in electrostatic capacitance. The surface polyimide porous membrane facing the air and the surface facing the substrate were different as a result of the manufacturing process. In order to investigate the difference, each film surface was observed with SEM. Furthermore, the ethanol
aqueous solution was applied dropwise to each surface and allowed to permeate, the permeability was calculated from the electrostatic capacitance, and the structure was estimated. The rings of the imide group were opened by alkaline treatment. The opened polyimide film was observed with electrical characteristics capable of measuring the permeation behavior of the solution in real time [16]. The relaxation time was calculated by obtaining Cole-Cole plots of membranes having different degrees of ring opening, and it was evaluated whether the molecular structure can be determined from the electric properties.

2. **Experimental**

2.1. Fabrication of porous polyimide membrane

The experiment was carried out with a porous polyimide membrane having a film thickness of 40 μm and a porosity of 70%. Silica fine particles were dispersed in a polyamic acid solution, this was applied to a substrate to form a membrane, the membrane was imidized, and the silica was removed with hydrofluoric acid, resulting in a porous membrane. Figure 1 shows the chemical reaction in which the imide group rings are opened by an alkaline solution. The membrane was immersed in an alkaline aqueous solution of TMAH 1.0 wt% and ethanol 40 wt% for 2 min to obtain membranes with a low degree of ring opening, and for 5 min to obtain membranes with a high degree of ring opening.

![Fig. 1. The ring opening of imide group upon alkaline treatment.](image)

2.2. Electrical property measurement

Electrodes were prepared by laminating a copper plate with thickness of 35 μm on a phenol resin plate with thickness of 1.6 mm. The dielectric properties were measured by sandwiching a polyimide porous membrane that was 20 mm long on each side between two electrodes and applying drops of 15 wt% ethanol aqueous solution through a 1 mm diameter hole drilled in one electrode. Figure 2 is a schematic diagram and a photograph showing the external appearance of the electrode. Dielectric characteristics were measured with an impedance analyzer (Hioki E.E. CORPORATION, LCRmeter IM3570, 4 Hz ~ 5 MHz).

First, the electrostatic capacitance change of the polyimide porous membrane was measured, and the permeability of the ethanol aqueous solution was calculated from the relation between the electrostatic capacitance and time. Next, the air-facing surface and the substrate-facing surface were observed with SEM, and the permeability of these surfaces to the ethanol aqueous solution was compared. Finally, the relaxation time of porous polyimide membranes with different degrees of ring opening was estimated from Cole-Cole plots assumed to be Debye’s semicircles.

3. **Results and discussion**

3.1. Capacitance and permeation rate

Permeation of ethanol into the porous membrane can be explained as due to concentration diffusion and capillary force. A schematic diagram of concentration diffusion is shown in Fig. 3 (A) and a schematic diagram of the capillary force is shown in Fig. 3 (B).

![Fig. 3. Schematic diagrams of the concentration diffusion (A) and the capillary force which ethanol aqueous solution permeation porous membrane (B).](image)

The capacitance measurements are presented in Fig. 4. The capacitance rapidly increased after drops of the ethanol aqueous solution started to be applied and then it gradually stabilized. The electrostatic capacitance is $C$, the electrostatic capacitance immediately after application of the ethanol aqueous solution starts is $C_{\text{ref}}$, and the steady capacitance level reached during application is $C_{\text{max}}$. The permeation rate of the solution into the porous membrane was calculated by the following equation.
permeation rate = \frac{C - C_{\text{ref}}}{C_{\text{max}} - C_{\text{ref}}} \tag{1}

Fig. 4. Capacitance of polyimide porous membrane in which ethanol aqueous solution was applied.

The relationship between permeation rate and time is shown in Fig. 5. Ethanol aqueous solution quickly permeated into 90% of the pores in the porous polyimide membrane in 110 seconds, and then gradually filled the whole membrane.

Fig. 5. Permeation rate of ethanol aqueous solution in porous membrane.

3.2. Permeability of membrane surface

SEM pictures of the air-facing surface and the substrate-facing surface of polyimide membrane are shown in Fig. 6. From these pictures, we can observe that the air-facing surface has openings with a larger area than the substrate-facing surface. Next, an ethanol aqueous solution was applied dropwise to the air-facing surface and to the substrate-facing surface, the capacitance was measured, and the permeation rate was calculated. Figure 7 is a graph of the relationship between permeation rate and time. The permeation rate was 3 times faster when drops of the ethanol aqueous solution were applied on the air-facing surface than on the substrate-facing surface. These results are to be expected considering that the air-facing surface has a larger surface area than the substrate surface, and that the contribution of capillary force to the permeability of the solution is high.

Fig. 6. SEM pictures of air-facing surface and substrate-facing surface of polyimide membrane.

Fig. 7. Permeation rate of ethanol aqueous solution in porous membrane.

3.3. Effect of ring-open imide group

Cole-Cole plots of porous membranes with different degrees of imide group ring openings caused by alkali treatment were estimated using Debye’s semicircle formula described as equation (2) [16]. Here, $\varepsilon'$ is dielectric constant, $\varepsilon''$ is dielectric loss, $\varepsilon_\infty$ is dielectric constant when measured frequency is extremely high and $\varepsilon_0$ is dielectric constant when measured frequency is 0 Hz. The results are shown in Fig. 8.

$$\left(\varepsilon' - \frac{\varepsilon_\infty - \varepsilon_0}{2}\right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_\infty - \varepsilon_0}{2}\right)^2 \tag{2}$$

Fig. 8. Capacitive semicircles of imide group membranes with different degrees of ring opening.

Unlike the membrane in which all of the imide group had closed rings, two capacitive semicircles in the ring-opened polyimide membrane could be confirmed. Moreover, it was found that the dielectric constant also increased with increase in the degree of ring opening. Figure 9 shows the results of complementing the capacitive semicircle of a membrane with a low ring opening degree by

Fig. 9. Relative dielectric constant and relative dielectric loss factor of membranes with different degrees of ring opening.
the least-square method. Figure 9 (A) is the enlargement of the left circle of the capacitive circle and (B) is the whole. From this graph, \( \tau \) (relaxation time) and \( \beta \) (relaxation time distribution constant) were calculated. The same calculation was carried out for membranes with high ring-opening degree. The results of the above are shown in Table 1. The relaxation time was longer as the degree of ring opening rose. It seems that strong ionic interaction of ring opening membrane makes polymer difficult to move. This indicates that changes in the molecular structure can be detected by examining the electrical properties of the porous membrane. In addition, \( \beta \) of the right circle of the ring-opened membrane was 1 or less, which is almost equal to that of ordinary solid polymers such as PET, PMMA and Nylon [17]. Relaxation time was longer than those polymers [17].

![Fig. 9. Complementing capacitive semicircle of low ring opening membrane (A) left side (B) right side.](image)

Table 1. Relationship between degree of ring-open imide group and electrical properties of membrane.

|                  | \( e_\varepsilon \) | \( e_\infty \) | \( \tau \) [ms] | \( \beta \) |
|------------------|----------------------|----------------|----------------|----------|
| Ring closing membrane | 0.81                | 0.014          | 0.17           | 1        |
| Low ring opening membrane | 249                | -0.016         | 0.23           | 1        |
| Left side semicircle    |                     |                |                |          |
| Low ring opening membrane | 23.42              | 1.025          | 12             | 0.547    |
| Right side semicircle   |                     |                |                |          |
| High ring opening membrane | 5.08               | -0.015         | 0.23           | 1        |
| Left side semicircle    |                     |                |                |          |
| High ring opening membrane | 47.67              | -0.626         | 75             | 0.493    |
| Right side semicircle   |                     |                |                |          |

4. Conclusion

We evaluated the permeability of a solution into polyimide porous membranes and the changes in the molecular structure of the membranes, based on their electrical properties. The capacitance rapidly increased as drops of ethanol aqueous solution were applied to the porous membrane, and then gradually reached a steady level. The permeation rate was calculated from the capacitance, and the permeation behavior of the ethanol aqueous solution into the porous membrane was estimated. We compared the air-facing surface and the substrate-facing surface of the porous membrane through SEM observation and permeability measurement, which revealed that the air-facing surface had a large opening area and high permeability. The imide group whose rings were opened by alkali treatment were found to have higher dielectric constant and longer relaxation time as the degree of ring opening increased. These results suggest that changes in the molecular structure of the membrane can be detected by measurement of electrical properties.

References
1. T. Sugawara, J. Koshiyama, and A. Kawai, *J. Photopolym. Sci. Technol.*, 31 (2018) 437.
2. S. Chisca, V. E. Musteata, I. Sava, and M. Bruma, *Eur. Polym. J.*, 47 (2011) 1186.
3. Y. Liu, Q. Chen, and X. Du, *Mater. Lett.*, 223 (2018) 207.
4. K. P. Yoo, M. J. Lee, K. H. Kwon, J. Jeong, and N. K. Min, *Thin Solid Films*, 518 (2010) 5986.
5. D. Jacobs, M. J. Arlen, D. H. Wang, Z. Ounaies, R. Berry, L. S. Tan, P. H. Garrett, and R. A. Vaia, *Polymer*, 51 (2010) 3139.
6. J. S. Moya, S. L. Esteban, and C. Pecharroman, *Prog. Mater. Sci.*, 52 (2007) 1017.
7. R. S. Dariani and F. Tavakoli, *Physica B*, 456 (2015) 312.
8. Y. G. Abreu, L. C. S. Gonzalez, A. P. Barranco, and J. D. S. Guerra, *J. Alloys Compd.*, 747 (2018) 38.
9. Z. N. Wing and J. W. Halloran, *Ceram. Int.*, 43 (2017) 4618.
10. C. Hamciuc, E. Hamciuc, M. Asandulesa, Y. Kalvachev, L. Dimitrov, and M. Ignat, *Mater. Res. Bull.*, 102 (2018) 70.
11. H. Li, Y. Qiu, and L. Duan, *Org. Electron.*, 33 (2016) 164.
12. A. Muto, Y. Hiraguchi, K. Kinugawa, T. Matsumoto, Y. Mizoguchi, and H. Tokumoto, *Colloids Surf. A: Physicochem. Eng. Asp.*, 506 (2016) 228.
13. K. Huang, L. Pan, and R. H. Yoon, *Miner. Eng.*, 115 (2018) 88.
14. J. Kamcev, C. M. Doherty, K. P. Lopez, A. J. Hill, D. R. Paul, and B. D. Freeman, *J. Memb. Sci.*, 566 (2018) 307.
15. M. Galizia, P. L. Manna, M. Pannico, G. Mensitieri, and P. Musto, *Polymer*, 55 (2014) 1028.
16. W. D. kingery, “Introduction to Ceramics”, John Wiley & Sons, U.S.A. (1976).
17. Y. Inuishi, “Yudentaigensyouron”, Denkigakaidaigakukouza, Japan (1973) (in Japanese).