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Gas diffusion and solubility in He$^+$-irradiated asymmetric polyimide membranes

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Abstract

In this study, the gas diffusion and solubility of the asymmetric polyimide membrane irradiated by He ions were investigated using a high vacuum apparatus equipped with a Baratron absolute pressure gauge at 76 cmHg and 35 °C. Specifically, we estimated their effects on the gas permeation properties of the asymmetric membranes. The asymmetric polyimide membranes were prepared by a dry–wet phase inversion process, and the surface skin layer on the membrane was irradiated by He ions at fluences of 1×10^{15} or 3×10^{15} ions/cm^2 at 150 keV. We demonstrated that the gas diffusion had a significant influence on the gas permeability and selectivity of the He$^+$-irradiated asymmetric membrane.

Keywords: Ion irradiation; Gas separation membrane; Asymmetric membrane

1. Introduction

Polymer membranes are considered to be effective for the separation of gaseous mixtures due to their high separation efficiency, low operating costs, and simple operation. The development of novel polymer membranes with even higher gas permeabilities and selectivities has received much attention [1,2]. However, many studies of the structure/permeability relationships of polymer membranes have led to trade-off correlations between the gas permeability and selectivity, which have become a major problem in realizing a gas separation process using polymer materials [3,4]. Recently, significant interest has focused on the syntheses of inorganic membranes for gas separation. Particularly, a carbon molecular sieve (CMS) membrane, which is synthesized by the pyrolysis of a polymer, is considered to be one of the candidates for a gas separation membrane [5–7]. However, CMS membranes are very brittle and fragile. Additionally, they require more careful handling, and the preparation of a thin CMS membrane is very difficult because of its poor mechanical properties. As a result, the gas permeances of CMS membranes were not very high.

Recently, we reported that an asymmetric polyimide membrane with an ultrathin and defect-free carbonized skin layer prepared by the modification of the skin surface using ion-beam irradiation had a high gas permeability and selectivity [8]. It is well known that ion-beam irradiation can directly modify the surface of a membrane and that the polymer surface irradiated under a high ion fluence is carbonized [9,10]. The asymmetric membrane with the carbonized skin layer was characterized by its toughness and good mechanical properties, and we demonstrated that the ultrathin and defect-free carbonized skin layer was able to realize both a high gas permeability and selectivity.

Gas permeation of the polymer membranes is well known to obey a solution–diffusion mechanism and the permeability coefficient can be expressed by the following diffusion and solubility coefficients:

$$P = DS \tag{1}$$

where P is the gas permeability coefficient, D is the gas diffusion coefficient, and S is the gas solubility coefficient. D is calculated from Eq. (2).

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$$D = \frac{L^2}{6\theta} \tag{2}$$

where L is the membrane thickness and θ is the time lag before establishing a steady-state straight line of gas permeability. That is, D can be determined from the steady-state rate of the gas permeation through the membrane and S can be found using Eq. (1). However, the time lag of the He^+-irradiated asymmetric polyimide membrane with a carbonized skin layer reported in a previous paper was so short that we could not calculate the diffusion and solubility coefficients using the time lag method.

The objective of this study is to elucidate the gas transport mechanism of the asymmetric polyimide membranes with the thin and defect-free carbonized skin layer. Specifically, we focused on the effects of the gas diffusion and solubility coefficients on the gas permeability and selectivity of the ion-irradiated asymmetric polyimide membranes. To determine both parameters, we prepared the asymmetric polyimide membranes derived from 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 3,3′-diaminodiphenylsulfone (DDS) because the oxygen permeability of the 6FDA–DDS membrane indicated approximately 17-times smaller value than that of a polyimide membrane (6FDA–6FAP) reported in a previous paper [8]. Additionally, in comparison with the skin layer thickness of the 6FDA–6FAP asymmetric membrane, the 6FDA–DDS asymmetric membrane was approximately 20-times thicker, indicating that the time lag of the 6FDA–DDS membrane is sufficiently long to calculate the gas diffusion coefficient. We prepared the asymmetric membranes with approximately 1.8 μm skin layer thickness using the dry–wet phase separation process. The gas permeances of the asymmetric polyimide membranes modified by He^+-irradiation with 150 keV at fluences of 1×10^{15} and 3×10^{15} ions/cm^2 have been measured using a high vacuum apparatus equipped with a Baratron absolute pressure gauge at 76 cmHg and 35 °C.

2. Experimental part

2.1. Materials

2,2′-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purchased from the Clariant Co. (Shizuoka, Japan) and purified by sublimation prior to use. The diamine monomer was 3,3′-diaminodiphenylsulfone (DDS), which was purchased from the Tokyo Kasei Co. (Tokyo, Japan) and recrystallized twice from ethanol prior to use.

The polyimide, 6FDA–DDS, was synthesized by chemical imidization of the poly(amic acid) precursors as reported in literature [11,12]. The structure of 6FDA–DDS is shown in Fig. 1. The synthesized 6FDA–DDS had an Mw of 7.4×10^4 with a polydispersity index of 2.4.

2.2. Preparation of asymmetric polyimide membranes

To determine the effects of the gas diffusion and solubility coefficients on the gas permeation properties of the He^+-irradiated asymmetric polyimide membrane, the membranes with an approximately 1.8 μm skin layer were prepared by a dry–wet phase inversion process [13–16]. The polyimide solutions were made from 15 wt% polyimide, 60 wt% methylene chloride, 19 wt% 1,1,2-trichloroethane, and 6 wt% 1-butanol. After being filtered and degassed, the polyimide solutions were cast on a glass plate with a doctor-blade and then air-dried for 15 s at room temperature. After evaporation, the membranes were coagulated in methanol, washed for 12 h, air-dried for 24 h at room temperature, and finally dried in a vacuum oven at 150 °C for 15 h to remove all of the residual solvents. The apparent skin layer thickness was 1.8 ± 0.02 μm.

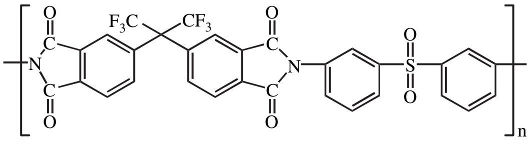


Fig. 1. Chemical structure of 6FDA–DDS polyimide.

2.3. Ion-beam irradiation on asymmetric membranes

Ion-beam irradiation is a physico-chemical surface-modification process resulting from the impingement of a high-energy ion beam (Riken ion implanter, Riken, Saitama, Japan) [17]. The ion depth through the top skin layer was regulated by changing the ion species and its energy. In this study, ion irradiation was performed on polyimide membranes and He^+ was used. The He^+-irradiation was carried out on a 2 × 2 cm^2 surface area at an energy of 150 keV and fluences of 1×10^{15} and 3×10^{15} ions/cm^2.

The glass transition temperature (T_g) was determined by differential scanning calorimetry (Seiko DSC200, SSC/5200H, Tokyo, Japan). The T_g of the asymmetric membrane before and after He ion irradiation was 332 °C. There was no great change in the thermogravimetric curves of the asymmetric membrane before and after He ion irradiation.

2.4. Surface characterization of asymmetric membranes

The surface change in the ion-irradiated polyimide membrane was measured by Fourier transform infrared spectroscopy combined with attenuated total reflectance (FTIR-ATR Nexus 470, Nicolet, Tokyo, Japan) and laser Raman spectroscopy (LabRam, Jobin Yvon, Tokyo, Japan). A square Ge crystal in an ATP objective was used, and 64 scans of 2 cm^{-1} resolution were averaged to achieve a sufficient signal-to-noise ratio. The Raman spectra were obtained using an He–Ne laser of 632.817 nm.

The surface morphology of the asymmetric polyimide membranes was visualized using an atomic force microscope (AFM, SPI3700, Seiko, Tokyo, Japan) in air at room temperature. Standard Si_3N_4 cantilevers (SN-AF01, Seiko, Tokyo, Japan), with a spring constant of 0.021 N/m, were used and operated in the non-contact mode. The surface was continuously imaged in the feedback mode with a scan area of

500 nm × 500 nm and at a constant scan speed of 2 Hz. The surface roughness parameter of the membranes was denoted by R_a, which is the arithmetic mean of departure of the roughness profile from the mean line.

2.5. Gas permeation measurements

The gas permeability coefficients of oxygen and nitrogen were measured with a high vacuum apparatus (Rika Seiki, Inc., K-315-H, Tokyo, Japan). The gas permeation measurements of the membranes were carried out at 35 °C and 76 cmHg. The apparent skin layer thickness of the asymmetric polyimide membranes was calculated from

$$L = \frac{P}{Q} \tag{3}$$

where L [cm] is the apparent skin layer thickness, P [cm^3(STP)cm/(cm^2 s cmHg)] is the gas permeability coefficient measured from a dense polyimide flat membrane, and Q [cm^3(STP)/(cm^2 s cmHg)] is the gas permeance of the asymmetric polyimide membranes. L was determined from the oxygen permeability coefficient.

The permeation parameters, D and S, of the ion-irradiated asymmetric membranes were calculated from Eqs. (1) and (2) using the time lag, θ.

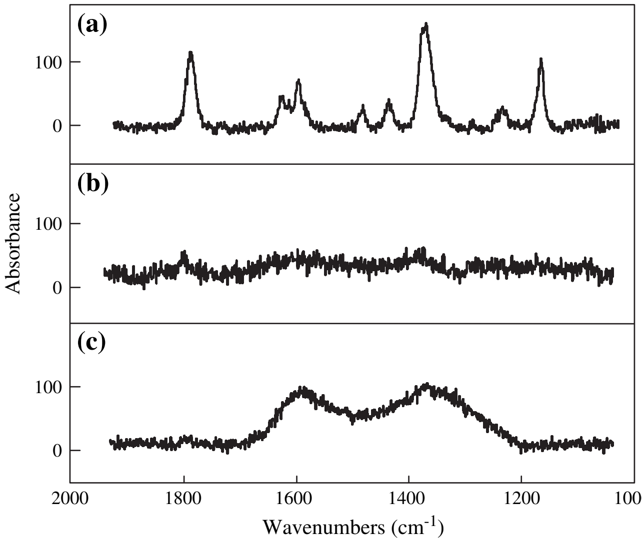


Fig. 2. Raman spectra of asymmetric polyimide membranes: (a) control; (b) He$^+$-irradiation at 1 × 10^{15} ions/cm^2; (c) He$^+$-irradiation at 3 × 10^{15} ions/cm^2.

3. Results and discussion

3.1. Surface characteristics of asymmetric membranes

Fig. 2 shows the Raman spectra of the asymmetric polyimide membranes irradiated at an energy of 150 keV and fluences of 1 × 10^{15} and 3 × 10^{15} ions/cm^2. After the irradiation of 1 × 10^{15} ions/cm^2, the peaks at 1150, 1230, 1360, 1570–1630, and 1780 cm^{-1} corresponding to C–S, C–F$_3$, C–N, C=C in the aromatic ring, and C=O, respectively, disappeared. The disappearance indicates the breaking of carbon binding such as aromatic and imide rings. Additionally, after irradiation of 3 × 10^{15} ions/cm^2, two broad peaks on the irradiated polyimide surface appeared at around 1360 and 1580 cm^{-1}. These peaks correspond, respectively, to the well-known D and G broad bands of disordered graphitic materials [18], indicating that the surface on the membrane changed to a carbon-enriched material. Particularly, the D and G broad band peaks for the 6FDA–DDS membrane irradiated at a fluence of 3 × 10^{15} ions/cm^2 were significantly greater than those of the 6FDA–6FAP membrane reported in a previous paper [8], indicating that the surface on the former would change to a more carbon-enriched material when compared to that on the latter.

Fig. 3 shows the ATR-FTIR spectra of the asymmetric polyimide membranes irradiated at 150 keV at fluences of 1 × 10^{15} and 3 × 10^{15} ions/cm^2. There was a significant difference in the absorbance between the membrane before ion irradiation as the control membrane and the irradiated membranes, and the absorbance intensities of the carbonyl (1730 cm^{-1}), S=O (1100 and 1150 cm^{-1}), CF$_3$ (1200–1250 cm^{-1}), imide (1380 cm^{-1}), and aromatic (1480 cm^{-1}) groups were significantly reduced. Simultaneously, a broad band appears in the region of 1550–1650 cm^{-1} based on the formation of graphite-like and carbon-rich amorphous structures and

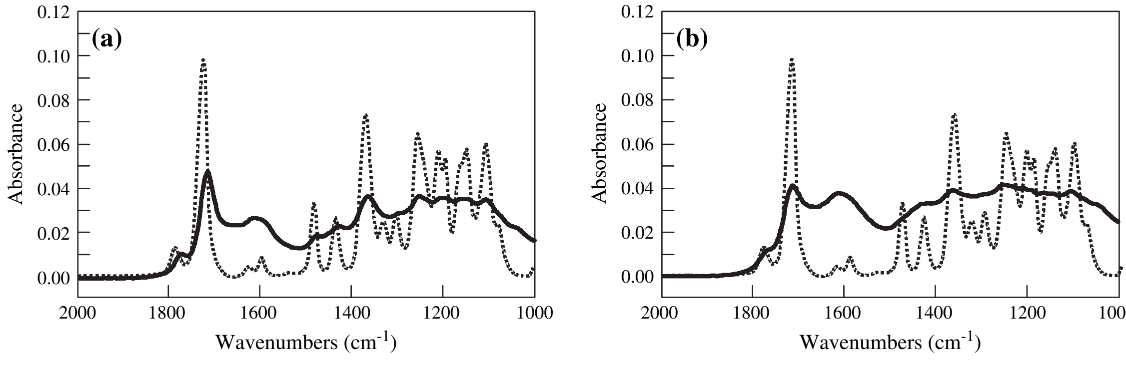
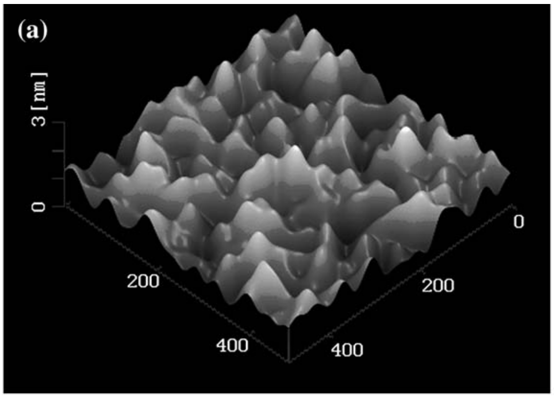
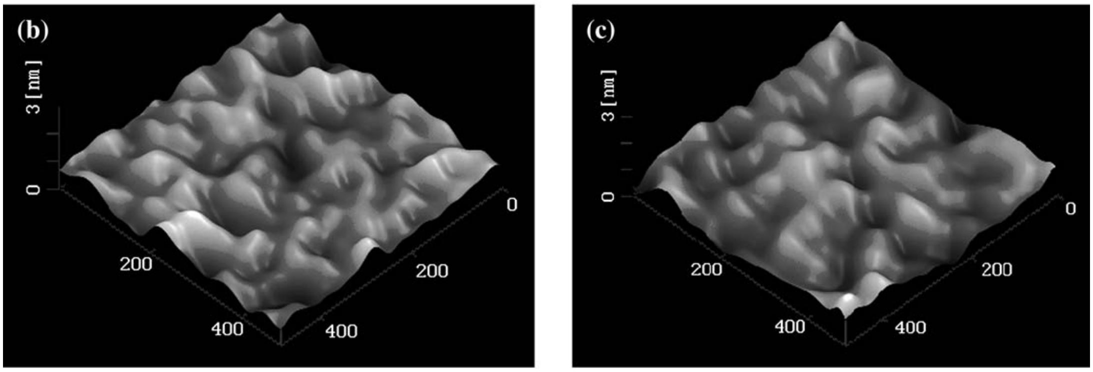


Fig. 3. ATR-FTIR spectra of asymmetric polyimide membranes: (a) (broken lines) control (solid lines) He$^+$-irradiation at 1 × 10^{15} ions/cm^2; (b) (broken lines) control (solid lines) He$^+$-irradiation at 3 × 10^{15} ions/cm^2.



Ra = 0.30 nm



Ra = 0.17 nm

Ra = 0.18 nm

Fig. 4. AFM images of top surface of asymmetric polyimide membranes. A scan area was 0.5 × 0.5 μm: (a) control; (b) He^+-irradiation at 1×10^{15} ions/cm^2; (c) He^+-irradiation at 3×10^{15} ions/cm^2.

the band intensities in the He^+-irradiated membranes at the fluence of 3×10^{15} ions/cm^2 were enhanced when compared to that of the membrane at 1×10^{15} ions/cm^2.

Fig. 4 shows the AFM image of the top surface of an asymmetric polyimide membrane in a three-dimensional form over an area of 500 nm × 500 nm. The surfaces of the He^+-irradiated polyimide membranes were smoother than that determined for an asymmetric polyimide membrane before ion irradiation as a control membrane. These results were similar to those reported in the previous papers [8]. However, there was no difference in the surface morphology between the membranes irradiated at fluences of 1×10^{15} and 3×10^{15} ions/cm^2.

3.2. Gas permeation properties of asymmetric membranes

Irradiating ions penetrating into a polymer membrane lose energy by several interactions between the ions and the polymer. The energy loss mechanism is considered to be an electronic energy loss, which involves the process of electronic excitation and ionization of the atoms in the polymers, as the exchanges of electrons between incident ions and the atoms in the polymer, and to be an nuclear energy loss, which involves atomic collisions between the incident ions and the atoms in the polymer [19]. The depth profiles of the energy loss for He^+-irradiation at 150 keV in the 6FDA–DDS asymmetric polyimide membrane were estimated using a well-established Monte Carlo simulation method (TRIM code). As is apparent from the He^+-depth in Fig. 5, the relative contribution of the electronic energy loss becomes greater for a thinner surface skin layer and that of the nuclear energy loss becomes greater for a thicker layer, and He^+ in the

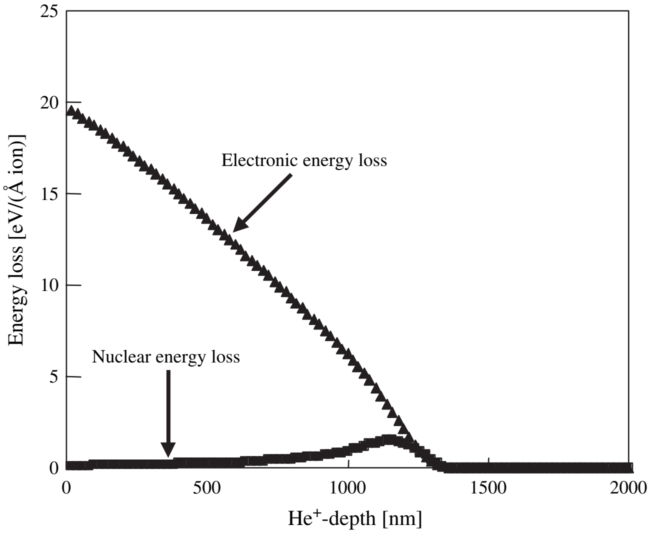


Fig. 5. Relationship between He^+-depth and energy loss in 6FDA–DDS polyimide.

6FDA–DDS membrane irradiated at 150 keV completely losses the electronic and nuclear energies at a 1.46 μm depth. We prepared the 6FDA–DDS asymmetric membrane with the skin layer thickness of approximately 1.8 μm, because the 1.8 μm thickness is of sufficient length to accurately measure the time lag before establishing a steady-state straight line of gas permeability. Therefore, the He^+-irradiated asymmetric membrane used in this study consists of two-layer surfaces, the non-irradiated and irradiated layers.

Table 1 shows the results of the oxygen permeability coefficient (P_{O_2}) and (O_2/N_2) selectivity of the asymmetric polyimide membranes with the skin layer thickness of approximately 1.8 μm at 35 °C and 76 cmHg. The 6FDA–DDS dense membrane as the control membrane indicated a P_{O_2} of 4.2×10^{-11} [cm^3(STP)cm/(cm^2 s cmHg)] as shown in Table 1. The apparent skin layer thickness of the asymmetric polyimide membrane before ion irradiation was calculated from the oxygen permeability coefficient of the dense membrane. The gas selectivities of the He^+-irradiated asymmetric membranes were greater than those ($O_2/N_2 = 7.5$) of a dense membrane, indicating that the permeation of the asymmetric membrane is predominantly carried out by a solution–diffusion mechanism and that the surface skin layer is essentially defect-free. Additionally, both the P_{O_2} and (O_2/N_2) selectivity of the asymmetric polyimide membranes were enhanced when compared with those of the dense membrane. It should be noted that the gas permeability and selectivity of the 6FDA–DDS asymmetric membrane were improved by the surface modification using ion-beam irradiation. Although the gas permeability coefficient of the asymmetric membrane irradiated at 3×10^{15} ions/cm^2 decreased more than that of the membrane at 1×10^{15} ions/cm^2, the gas selectivity of the former increased more than that of the latter, which may be due to the fact that the surface on the former membrane changed to a more carbon-enriched material, as apparent from the Raman spectral results.

Table 2 shows the results of the gas diffusion and solubility coefficients of the asymmetric polyimide membranes for O_2 and N_2 at 35 °C and 76 cmHg. Both the D_{O_2} and D_{N_2} values of the He^+-irradiated asymmetric membranes were greater than those of a dense membrane. The increase in the gas diffusion indicates a more open molecular structure in the He^+-irradiated asymmetric membranes than in the dense membrane. This is because the functional groups from the polyimide were eliminated by the He^+-irradiation, as is apparent from the results of the ATR-FTIR and Raman spectra of the He^+-irradiated asymmetric membranes. However, D_{O_2} value of the asymmetric membrane irradiated at 3×10^{15} ions/cm^2 was lower when compared with that of the membrane irradiated at 1×10^{15} ions/cm^2. We believe that the skin layer irradiated at 3×10^{15} ions/cm^2 changed to a more carbon-enriched material, as apparent from the Raman spectral results, so that the gas diffusion through the layer was suppressed. The gas diffusivity selectivities of the He^+-irradiated asymmetric membranes also significantly changed from the dense membrane. These findings suggest that the carbonized skin layer provides a high size and shape discrimination between gas molecules.

Table 1
Effect of He^+ influence on gas permeability coefficient and selectivity of asymmetric polyimide membranes at 35 °C and 76 cmHg

Acceleration energy (keV)	Ion fluence (ions/cm^2)	P_{O_2}	P_{N_2}	P_{O_2}/P_{N_2}
Control[a]	–	4.2	0.56	7.5
150	1×10^{15}	8.7	1.1	7.7
150	3×10^{15}	6.7	0.85	7.9

[a] Thickness = 35 μm, P: 10^{-11} [cm^3(STP)cm/(cm^2 s cmHg)].

Table 2
Effect of He^+ influence on gas diffusion and solubility coefficient of asymmetric polyimide membranes at 35 °C and 76 cmHg

Acceleration energy (keV)	Ion fluence (ions/cm^2)	D_{O_2}	D_{O_2}/D_{N_2}	S_{O_2}	S_{O_2}/S_{N_2}
Control[a]	–	2.4	5.9	0.17	1.3
150	1×10^{15}	7.7	6.8	0.11	1.1
150	3×10^{15}	5.5	6.8	0.12	1.1

[a] Thickness = 35 μm, D: 10^{-8} [cm^2/s], S: 10^{-2} [cm^3(STP)/cm^3 cmHg].

In contrast, S_{O_2} and S_{N_2} of the He^+-irradiated asymmetric membranes decreased when compared to those of a dense membrane. This may be due to the fact that functional groups, such as the CF_3 group, which are considered as influencing the gas solubility, were eliminated by the He^+-irradiation. However, S_{O_2} value of the asymmetric membrane irradiated at 3×10^{15} ions/cm^2 was greater than that of the membrane irradiated at 1×10^{15} ions/cm^2. It is well known that rearrangement of atoms on the polymer irradiated occurs under high ion fluence. We believe that the rearrangement may have influence on the gas solubility of the He^+-irradiated asymmetric membranes. However, the above arguments require validation by the structural analysis of the He^+-irradiated skin layer. The gas solubility selectivities of the asymmetric membranes also slightly declined more than those of the dense membrane. These findings indicated that the higher gas diffusivity selectivity was the principal factors that dominate in the determination of the gas selectivity of the He^+-irradiated asymmetric membrane.

Additionally, we determined the gas diffusion and solubility coefficients of the ion-irradiated skin layer using the following equations. The apparent thickness of the He^+-irradiated asymmetric membrane and the He ion depth in the membrane were 1.8 μm and 1.46 μm, respectively, indicating that the asymmetric membrane consisted of two-layer surfaces, the non-irradiated and irradiated skin layers, as shown in Fig. 6. The gas permeability through the two-layer surfaces was calculated using a simple resistance model.

$$\frac{L}{P} = \frac{L_N}{P_N} + \frac{L_I}{P_I} \tag{4}$$

$$L = L_N + L_I \tag{5}$$

where P, P_N, and P_I are the total gas permeability coefficient, the apparent gas permeability coefficient through the non-irradiated layer, and the apparent gas permeability coefficient

Fig. 6. Simple resistance model of gas permeability through the two-layer surfaces in ion-irradiated asymmetric polyimide membrane.

through the irradiated layer, respectively. L_N and L_I were the apparent thicknesses of the non-irradiated and irradiated layers, respectively.

The gas solubility of the two-layer surfaces was calculated using the following simple equation.

$$S = S_N + S_I \qquad (6)$$

where S, S_N, and S_I are the total gas solubility coefficient, the apparent gas solubility coefficient for the non-irradiated layer, and the apparent gas solubility coefficient for the irradiated layer, respectively. D_N and D_I, which are the apparent gas diffusion coefficient through the non-irradiated layer and the apparent gas diffusion coefficient through the irradiated layer, respectively, were calculated using Eqs. (1) and (6).

Table 3 shows the results of the P_{O_2} and (O_2/N_2) selectivity of the He^+-irradiated layer calculated using the simple resistance model. The P_{O_2} of the skin layer irradiated at 1×10^{15} ions/cm^2 and 3×10^{15} ions/cm^2 resulted in 126% and 119% increase, respectively, when compared to those for the He^+-irradiated asymmetric membrane shown in Table 1. On the other hand, the gas selectivity of the irradiated skin layer only slightly changed.

Table 4 shows the results of the gas diffusion and solubility coefficients of the He^+-irradiated layer for O_2 and N_2 at 35 °C and 76 cmHg. The D_{O_2} of the skin layer irradiated at 1×10^{15} ions/cm^2 and 3×10^{15} ions/cm^2 resulted in 142% and 136% increase, respectively, when compared to those for the He^+-irradiated asymmetric membrane shown in Table 2. This increase is considered to be due to a more open molecular structure formed by the He^+-irradiation, and, as the result, the gas diffusivity selectivity slightly increased. In contrast, the S_{O_2} and gas solubility selectivity in the irradiated layer was almost similar to that for the He^+-irradiated asymmetric membrane.

Table 3
Effect of He^+ influence on gas permeability coefficient and selectivity of carbonized skin layer at 35 °C and 76 cmHg

Acceleration energy (keV)	Ion fluence (ions/cm^2)	P_{O_2}	P_{N_2}	P_{O_2}/P_{N_2}
Control[a]	–	4.2	0.56	7.5
150	1×10^{15}	11	1.4	7.9
150	3×10^{15}	8.0	1.0	8.0

[a] Thickness = 35 μm, P: 10^{-11} [cm^3(STP)cm/(cm^2 s cmHg)].

Table 4
Effect of He^+ influence on gas diffusion and solubility coefficient of carbonized skin layer at 35 °C and 76 cmHg

Acceleration energy (keV)	Ion fluence (ions/cm^2)	D_{O_2}	D_{O_2}/D_{N_2}	S_{O_2}	S_{O_2}/S_{N_2}
Control[a]	–	2.4	5.9	0.17	1.3
150	1×10^{15}	11	7.2	0.10	1.1
150	3×10^{15}	7.5	7.4	0.11	1.1

[a] Thickness = 35 μm, D: 10^{-8} [cm^2/s], S: 10^{-2} [cm^3(STP)/cm^3 cmHg].

The asymmetric polyimide membrane prepared by ion-beam irradiation resulted in increases in the gas permeability and selectivity when compared with those of the control membrane before ion irradiation. Particularly, the P_{O_2} of the skin layer irradiated at 1×10^{15} ions/cm^2 indicated several times greater value than that for the control membrane. We demonstrated that the gas diffusivity through the modified skin layer formed by ion irradiation had significant influence on the gas permeability of the He^+-irradiated asymmetric membrane. However, the gas selectivity of the He^+-irradiated skin layer only slightly increased when compared with that of the control membrane, and in comparison with that of the carbon molecular sieve (CMS) membranes, which are synthesized by the pyrolysis of a polymer, that of the He^+-irradiated asymmetric membrane was not high value. It is well known that the gas selectivities of the CMS membranes prepared at high pyrolysis temperature show several times greater values when compared with those determined in the polymer precursors before the pyrolysis process. However, the gas permeabilities of the CMS membranes are lower than those of the polymer precursors. That is, the results obtained in this study may indicate that the gas transport properties of the ion-irradiated asymmetric polyimide membranes show a good balance between the gas permeability and selectivity rather than those of the CMS membranes.

4. Conclusion

In this study, we investigated the gas diffusion and solubility of the He^+-irradiated asymmetric polyimide membranes and clarified their effects on the gas permeation properties of the asymmetric membranes. We demonstrated that the increase in the gas permeability was a result of the gas diffusion through the He^+-irradiated asymmetric polyimide membrane, while the gas solubility only slightly changed between the He^+-irradiated asymmetric polyimide membrane and the dense membrane. Additionally, it was clarified that the increase in the gas selectivity was a result of the gas diffusion selectivity in the asymmetric membrane. These findings indicated that the gas diffusion space, which can provide a high size and shape discrimination between the gas molecules, was formed in the ion-irradiated skin surface and suppressed the diffusion of N_2 rather than that of O_2.

Finally, it is desirable to prepare a polymer membrane with both a high gas permeability and selectivity for gas separation. We consider that ion irradiation would be one of the important membrane fabrication techniques for realizing a high gas permeability and selectivity. To prepare such membranes, an ion-irradiated membrane having a gas diffusion space like molecular sieves deserves further study.

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