Gas Permeation Properties of Asymmetric Polyimide Membranes with Partially Carbonized Skin Layer

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ABSTRACT: In this study, the gas permeance and selectivity of the asymmetric polyimide membrane irradiated by He ions were measured using a high vacuum apparatus with a Baratron absolute pressure gauge at 76 cmHg and 35 °C. The asymmetric polyimide membranes were prepared from a dry−wet phase inversion process, and the surface skin layer on the membrane was irradiated by He ions in the fluence range from 1×10^{12} to 3×10^{15} (He^+/cm^2) at 50 keV. We demonstrated that the gas selectivity of the He^+-irradiated membrane increased with an increase in the ion fluence and that the depth profile of the energy loss for the irradiating ions in the skin layer had a significant influence on the gas permeability and selectivity of the asymmetric membrane.

Introduction

The gas separation process using polymer membranes has received much attention, because the membrane systems provide better energy efficiency than conventional separation methods.[1,2] Many polymers have been synthesized to control the gas permeability and selectivity of the polymer membranes, because the ability to achieve such control provides a good understanding of the relationships between the chemical structure of polymers and the gas permeation property.[3,4] However, many studies of the structure/permeability relationships of polymer membranes have led to tradeoff correlations between the gas permeability and selectivity, which have become a major problem in realizing a gas separation process using polymer materials. Therefore, an important objective for the use of gas separation membranes is the development of new polymer membranes combining high gas permeability and selectivity.

Recently, a great interest has been noted in the syntheses of inorganic membranes for gas separation. One of the candidates is a carbon molecular sieve (CMS) membrane, which is synthesized by the pyrolysis of a polymer.[5,6] Suda reported that the CMS membrane prepared by the pyrolysis of Kapton polyimide membranes exhibited high gas selectivities, which were H_2/N_2 4700, CO_2/N_2 122, and O_2/N_2 36.[5] However, CMS membranes are very brittle and fragile. Additionally, they require more careful handling, and it is very difficult to prepare a thin CMS membrane because of its poor mechanical property. Therefore, the gas permeances of CMS membranes were not very high.

On the other hand, we reported the gas permeability through an asymmetric polyimide membrane with a thin and defect-free skin layer prepared by a dry−wet phase inversion process.[7−11] We succeeded in preparing an asymmetric polyimide membrane with an ultrathin and defect-free skin layer (10 nm) having a significantly high gas permeance. Additionally, we reported that the gas selectivities of an asymmetric polyimide membrane with a defect-free skin surface oriented by shear stress without a coating process increased with an increase in the molecular orientation of the polyimide.[10,11] This result indicates that an asymmetric membrane with a modified ultrathin and defect-free skin layer would enhance both the gas permeability and selectivity.

In this paper, we describe an organic−inorganic hybrid membrane, which exhibits an asymmetric structure consisting of a carbonized skin layer and a polymeric porous substructure, used to synthesize a novel gas separation membrane combining high gas permeability and selectivity. It is well-known that ion-beam irradiation can directly modify the surface of a membrane and that the polymer surface irradiated with high ion fluence is carbonized.[12,13] This means that the ion irradiation can only carbonize a thin surface skin layer, while the pyrolysis of a polymer at high-temperature degrades the entire volume. Marletta reported the surface carbonization of a polyimide irradiated with 150 keV Ar^+ at a fluence greater than 5×10^{15} ions/cm^2.[14] The permeation behavior of the gas through the ion-irradiated polymer membrane was also investigated. Xu reported the gas permeability of a polyimide−ceramic composite membrane or asymmetric polysulfone membrane irradiated by H^+ at a low fluence.[15,16] Won also reported the gas permeability of a thick polymer dense membrane irradiated at a high ion fluence.[17] We prepared an asymmetric polyimide membrane with a thin skin layer carbonized by the ion-beam irradiation. The asymmetric membrane with the carbonized skin layer is characterized by being tough and having a good mechanical property, and we consider that the ultrathin and defect-free carbonized skin layer would realize both a high gas permeability and selectivity.

The objective of our study is to fabricate a novel asymmetric polyimide membrane with an ultrathin and defect-free carbonized skin layer. In this preliminary study, the gas permeances of the asymmetric polyimide membranes irradiated with 50 keV He^+ at fluences less than 3×10^{15} ions/cm^2 have been measured using a high vacuum apparatus with a Baratron absolute pressure gauge at 76 cmHg. In particular, we focused on the permeation properties of the gas through the partially

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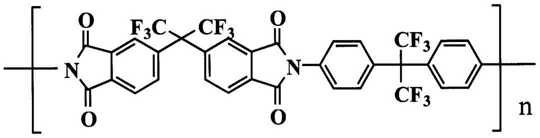
Scheme 1. Chemical Structure of 6FDA−6FAP Polyimide



carbonized skin layer prepared using low irradiation energy and fluence, because the partially carbonized membrane prepared by pyrolysis is reported to show a good balance between the gas permeability and selectivity when compared with the finally pyrolyzed membrane.[6] Additionally, the temperature dependence of the gas permeability through the asymmetric membrane and the effects of the ion-irradiated skin layer thickness on the gas permeation properties are also discussed in this study.

Experimental Section

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 2,2′-bis(4-aminophenyl)hexafluoropropane (6FAP), which was purchased from the Central Glass Co., (Saitama, Japan) and recrystallized twice in ethanol prior to use.

The polyimide, 6FDA−6FAP, was synthesized by chemical imidization of the poly(amic acid) precursors as reported in the literature.[18,19] The structures of 6FDA−6FAP are shown in Scheme 1. The synthesized 6FDA−6FAP had an M_w of 3.2 $\times$ 10^5 with a polydispersity index of 2.1.

Preparation of Asymmetric Polyimide Membranes. To investigate the effects of the skin layer thickness on the gas permeation properties of the asymmetric polyimide membrane, membranes with a different skin layer, approximately 80 nm and 4 μm, were prepared by a dry/wet phase inversion process.[7,8,20] The polyimide solutions for the 80 nm skin layer were made from 14 wt % polyimide, 61 wt % methylene chloride, 17.5 wt % 1,1,2-trichloroethane, and 7.5 wt % 1-butanol, and the solutions for the 4 μm skin layer were made from 11 wt % polyimide, 59 wt % methylene chloride, 21 wt % 1,1,2-trichloroethane, and 9 wt % methanol. After being filtered and degassed, the polyimide solutions were cast on a glass plate by 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.

Ion-Beam Irradiation on Asymmetric Membranes. Ion-beam irradiation is a physicochemical surface-modification process resulting from the impingement of a high-energy ion beam (Riken ion implanter, Riken, Saitama, Japan).[21] The ion depth through the top skin layer was regulated by changing the ion speciesand its energy. In this study, ion irradiation was performed on polyimide membranes and He^+ was used. Ion irradiation was carried out on a 2 $\times$ 2 cm^2 surface area at an energy of 50 keV with a fluence ranging from 1 $\times$ 10^{12} to 3 $\times$ 10^{15} ions/cm^2.

Surface Characterization of Asymmetric Membranes. The cross sections of the asymmetric polyimide membranes were observed using a scanning electron microscope (SEM, JXP-6100P, JEOL, Tokyo, Japan).

The surface morphology of the asymmetric polyimide membranes was visualized by 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 noncontact mode. The surface was continuously imaged in the feedback mode with a scan area of 1.5 μm $\times$ 1.5 μm and at a constant scan speed of 2 Hz. The surface roughness parameter of the membranes was denoted by R_a, which is an arithmetic mean of departure of the roughness profile from the mean line.

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 sixty-four scans of 2 cm^{-1} resolution were averaged to achieve a sufficient signal-to-noise ratio. The Raman spectra were observed using an He−Ne laser of 632.817 nm.

Gas Permeation Measurements. Gas permeances of carbon dioxide, oxygen, methane, 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

$$L = \frac{P}{Q} \qquad (1)$$

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 the 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.

Results and Discussion

Surface Characteristics of Asymmetric Membranes. Figure 1 shows the results of the SEM observations of the asymmetric polyimide membranes before and after ion irradiation. The apparent skin layer thickness of the membrane was calculated from the oxygen permeability coefficient, and the calculated thickness was approximately 80 nm. Ion irradiation was carried out on the polyimide surface at an energy of 50 keV He^+ with a fluence of 3 $\times$ 10^{15} ions/cm^2 at room temperature. The cross sectional structure of the asymmetric membrane consisted of an ultrathin skin layer and a porous substructure characterized by the presence of finger voids. There was no significant difference in the cross sectional structure between the virgin and irradiated asymmetric membranes.

Figure 2 shows the AFM image of the top surface of an asymmetric polyimide membrane in a three-dimensional form over an area of 1.5 μm $\times$ 1.5 μm. He^+ irradiation was carried out on the polyimide surface at 50 keV with a fluence of 3 $\times$ 10^{15} ions/cm^2. The difference in the morphology is evaluated by the roughness parameter, R_a. The R_a values of the asymmetric membranes before and after the ion irradiation were 0.86 and 0.47 nm, respectively, and the roughness on the surface decreased with an increase in the irradiation fluence. Our results obtained in this study were similar to those reported in the previous papers.[13,21]

The changes in the chemical structures of the He^+-irradiated polyimide surface were analyzed by attenuated total reflection. Figure 3 shows the ATR−FTIR spectra of the asymmetric polyimide membranes before and after ion irradiation. The He^+ irradiation was carried out on the polyimide surface at 50 keV with a fluence of 3 $\times$ 10^{15} ions/cm^2. The normal line represents the spectrum of the virgin asymmetric membrane, and the bold line represents the spectrum of the irradiated asymmetric membrane. There was a significant difference in the absorbance between the virgin and irradiated membranes. Ion-beam irradiation induced changes in the chemical structure of the polyimide surface, and

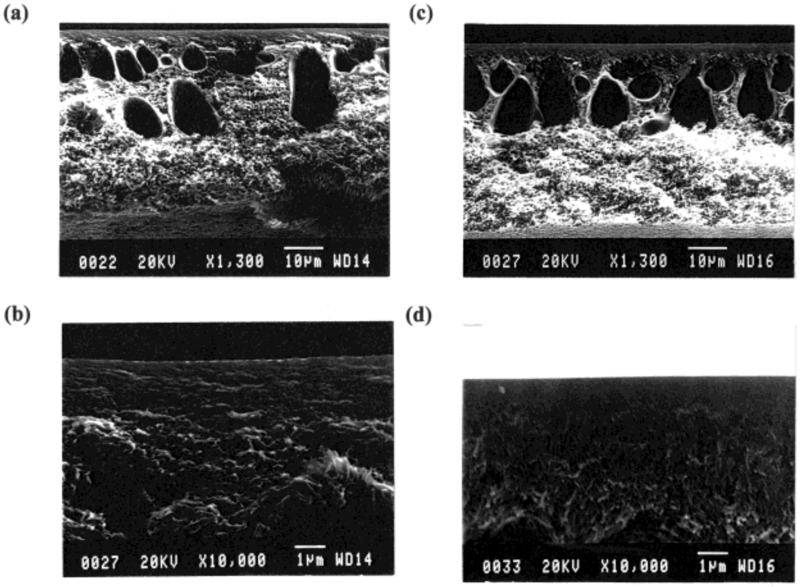


Figure 1. SEM photographs of cross section of the asymmetric polyimide membranes: (a) virgin membrane × 1300; (b) virgin membrane × 10000; (c) He^+-irradiated membrane × 1300; (d) He^+-irradiated membrane × 10000. He^+-irradiation was carried out at 3×10^{15} ions/cm^2. The apparent skin layer thickness was approximately 80 nm

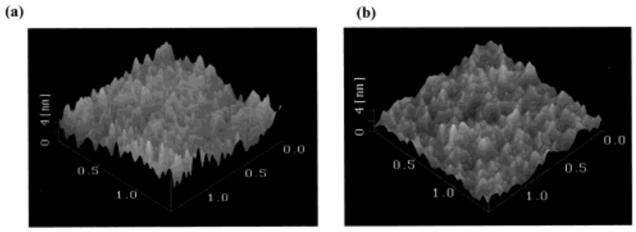


Figure 2. Three-dimensional AFM images of top surface of the asymmetric polyimide membranes. A scan area was 1.5 μm × 1.5 μm: (a) virgin membrane; (b) He^+-irradiated membrane. He^+-irradiation was carried out at 3×10^{15} ions/cm^2.

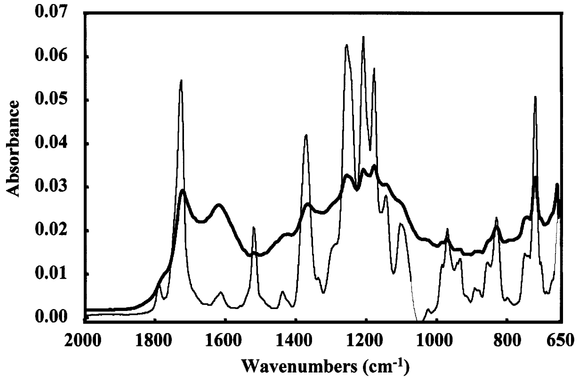


Figure 3. ATR−FTIR spectra of asymmetric polyimide membranes: (–) virgin; (**—**) He^+-irradiation at 3×10^{15}ions/cm^2.

the changes strongly depended on the ion fluence. The spectra show the changes in the characteristic absorbance of the carbonyl (1720 cm^{-1}), CF_3 (1200−1250 cm^{-1}), imide (1376 cm^{-1}), and aromatic (1500 cm^{-1}) groups. The absorbance intensities were significantly reduced.

Figure 4 shows the Raman spectra of the asymmetric polyimide membranes irradiated by a 50 keV He^+ with 1×10^{15} and 3×10^{15} ions/cm^2. The peaks at 1240, 1380, 1620, and 1780 cm^{-1} correspond to C−F_3, C−N, and C=C in the aromatic ring, and C=O, respectively. After the irradiation of a 50 keV He^+ at a fluence of 1×10^{15} ions/cm^2, these peaks on the polyimide surface disappeared. However, two broad peaks on the polyimide surface irradiated at a fluence of 3×10^{15} ions/cm^2 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,[23] indicating that the surface on the membrane changed to a carbon-enriched material.

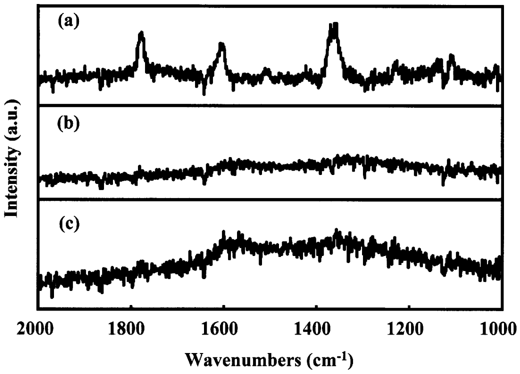


Figure 4. Raman spectra of asymmetric polyimide membranes: (a) virgin; (b) He^+-irradiation at 1×10^{15} ions/cm^2; (c) He^+-irradiation at 3×10^{15} ions/cm^2.

Gas Permeation Properties of Asymmetric Membranes. The results of the gas permeance and selectivity of the asymmetric polyimide membranes for CO_2, O_2, N_2, and CH_4 at 35 °C and 76 cmHg are shown in Table 1. The He^+ fluence ranges were from 1×10^{12} to 3×10^{15} (ions/cm^2). The virgin asymmetric membrane indicated an O_2 permeance of 8.0×10^{-5} [cm^3(STP)/(cm^2 s cmHg)], and the mean skin layer thickness calculated from the oxygen permeability coefficient was 80 ± 3.7 nm. The gas selectivities of all the asymmetric membranes were similar to or greater than those (O_2/N_2 = 4.5 and CO_2/CH_4 = 29) of a dense membrane, which indicates 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.

The depth profiles of the energy loss for He^+ irradiation at 50 keV in the asymmetric polyimide membrane were estimated using a well-established Monte Carlo

Table 1. Effect of He^+ Fluence on Gas Permeance and Selectivity of He^+-Irradiated Asymmetric Polyimide Membranes at 35 °C and 76 cmHg[a]

He^+ fluence (ions/cm^2)	Q_{O_2}	Q_{CO_2}	Q_{O_2}/Q_{N_2}	Q_{CO_2}/Q_{CH_4}
virgin	8.0	28	4.8	30
1×10^{12}	10.0	35	4.8	32
1×10^{13}	10.0	37	4.6	32
1×10^{14}	7.4	27	4.6	30
1×10^{15}	5.4	22	6.7	59
3×10^{15}	3.3	15	7.8	79

[a] Apparent skin layer thickness is 80 ± 3.7 nm. $Q = 10^{-5}$ cm^3(STP)/(cm^2 s cmHg).

simulation method (TRIM code). The mean projected range of the He ions in the membrane was 975 nm, and the energy loss was relatively flat over a large portion of the depth range. That is, He ions are considered to have completely penetrated through the skin layer in the asymmetric polyimide membrane, because the apparent skin layer thickness was approximately 80 nm.

Both the gas permeance and selectivity of the asymmetric polyimide membranes strongly depended on the He^+ fluence, as shown in Table 1. The O_2 and CO_2 permeances of the asymmetric membranes irradiated at the fluence of less than 1×10^{13} (ions/cm^2) increased when compared with the asymmetric membrane before the ion irradiation. In contrast, the permeances of the asymmetric membranes irradiated at the fluence of more than 1×10^{14} (ions/cm^2) decreased with an increase in the He^+ fluence. In particular, the asymmetric membrane irradiated at 3×10^{15} (He^+/cm^2) indicated significantly decreased gas permeances, and the O_2 and CO_2 permeances in the membrane showed 59% and 48% reductions, respectively, when compared with those of the asymmetric membrane before ion irradiation. On the other hand, the (O_2/N_2) and (CO_2/CH_4) selectivities in the asymmetric membrane irradiated at the fluence of more than 1×10^{14} (ions/cm^2) increased with an increase in the He^+ fluence. It should be noted that the (O_2/N_2) and (CO_2/CH_4) selectivities in the asymmetric membrane irradiated at 3×10^{15} (He^+/cm^2) resulted in 63% and 163% increases, respectively, when compared with those of the asymmetric membrane before ion irradiation.

Generally, the more common polymer membranes show a decreasing trend of polymer selectivity with increasing permeability. CMS membranes also lead to the tradeoff correlations between the gas permeability and selectivity. Singh-Ghosal reported that the partially carbonized polyimide membranes during pyrolysis showed a significantly high gas permeability compared with the virgin polyimide membrane and that the finally pyrolyzed membrane did a large increase in the gas selectivity with the low gas permeability.[6] The behaviors of the gas permeability and selectivity of the He^+-irradiated asymmetric polyimide membranes were also similar to those of the CMS membranes.

To elucidate the gas permeation properties of the He^+-irradiated asymmetric membrane, the gas permeation measurements for CO_2, O_2, N_2, and CH_4 were carried out over the temperature range of 15−45 °C. Activation energies for the permeance (ΔE_p) of the asymmetric polyimide membranes are shown in Table 2. Interestingly, the ΔE_ps for O_2 and CO_2 in the irradiated asymmetric membranes showed minimum values at a fluence of 1×10^{13} (He^+/cm^2), which was in accordance with the highest O_2 and CO_2 permeances of the irradiated asymmetric membrane. These findings suggest that the increase in the gas permeability indicates the formation of a more open space for the permeation of gas molecules in the asymmetric membrane irradiated at a low fluence. It should be noted that the ΔE_ps of the four gas permeabilities significantly increased between 1×10^{13} and 1×10^{14} (He^+/cm^2). Additionally, a large increase in ΔE_ps for O_2 and CO_2 was also observed between 1×10^{14} and 1×10^{15} (He^+/cm^2), which was in accordance with an increase in the gas selectivity of the irradiated asymmetric membranes. That is, the ΔE_p in the irradiated asymmetric membrane increased when the degree of carbonization in the skin layer increased. Stiffer polymers generally behave more like "molecular sieves",[24] so that the permeability to gases decreases in the order $PCO_2 > PO_2 > PN_2 > PCH_4$; this is the order of increasing "kinetic diameter" of the penetrant molecules. The mobilities of N_2 and CH_4, which have larger kinetic molecular diameter, might be suppressed by the molecular sieving-like effect of surface carbonization from the early stage formed at a fluence of 1×10^{14} (He^+/cm^2), while O_2 and CO_2 showing smaller kinetic diameters maintained their mobilities with a 1×10^{15} (He^+/cm^2) fluence. The molecular sieving-like effect induced by the surface carbonization has a significant influence on the gas permeability and selectivity, indicating that a skin layer, which is beginning to carbonize, forms a barrier to gas permeability and provides a high size and shape discrimination between the gas molecules.

Table 2. Effect of He^+ Fluence on Activation Energy for Gas Permeance of He^+-Irradiated Asymmetric Polyimide Membranes at 76 cmHg[a]

He^+ fluence (ions/cm^2)	ΔE_p (kcal/mol)			
	N_2	O_2	CH_4	CO_2
virgin	3.3	2.5	3.8	0.75
1×10^{12}	3.4	2.1	3.5	0.53
1×10^{13}	3.2	1.9	4.0	0.39
1×10^{14}	4.1	2.6	4.7	1.3
1×10^{15}	4.2	3.5	4.7	2.0
3×10^{15}	4.1	3.5	4.8	2.0

[a] Apparent skin layer thickness is 80 ± 3.7 nm.

According to the solution-diffusion mechanism, ΔE_p can be expressed as a function of the heat of sorption (ΔH_s) and the diffusion activation energy (ΔE_d) as follows:

$$\Delta E_p = \Delta H_s + \Delta E_d \qquad (2)$$

However, in the asymmetric polyimide membrane, the time lag before establishing steady-state straight line of gas permeability was so short that we could not calculate the diffusion and solubility coefficients using the time lag. In general, ΔE_p of the glass polymer membrane strongly depends on ΔE_d. Singh-Ghosal also reported that the ΔE_d values for O_2 and N_2 in the CMS membrane increased when the degree of pyrolysis increased and that the high ΔE_p in the CMS membrane was responsible for the increased resistance to the gas diffusion in the pyrolyzed polymer matrix.[6] We believe that, as indicated from the results of ΔE_p in Table 2, the gas permeation properties, such as the diffusion and solubility, in the asymmetric polyimide membrane with the carbonized skin layer show a similar trend as those of the CMS membrane.

Additionally, we investigated the effects of the ion-irradiated skin layer thickness on the gas permeability

Table 3. Gas Permeance and Selectivity of He^+-Irradiated Asymmetric Polyimide Membranes at 35 °C and 76 cmHg[a]

He^+ fluence (ions/cm^2)	Q_{O_2}	Q_{CO_2}	Q_{O_2}/Q_{N_2}	Q_{CO_2}/Q_{CH_4}
virgin	1.7	7.0	4.9	35
3×10^{15}	2.2	10.0	5.2	43

[a] Apparent skin layer thickness is 3880 nm. $Q = 10^{-6}$ cm^3(STP)/(cm^2 s cmHg).

Table 4. Gas Permeability Coefficient and Selectivity of Carbonized Layer of He^+-Irradiated Asymmetric Polyimide Membranes at 35 °C and 76 cmHg[a]

	PO_2	PN_2	PO_2/PN_2
virgin polyimide layer	6.4	1.3	4.9
carbonized layer	103.0	6.3	16.0

[a] Apparent skin layer thickness is 3880 nm. $P = 10^{-10}$ cm^3(STP)cm/(cm^2 s cmHg)/

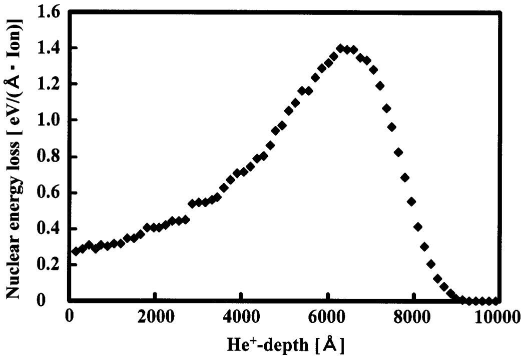


Figure 5. Relationship between He^+-depth and nuclear energy loss in the polyimide membrane.

and selectivity. The gas permeance and selectivity in the asymmetric membrane with an apparent thickness of 3880 nm are shown in Table 3. He^+ irradiation was carried out on the polyimide surface at 50 keV with a fluence of 3×10^{15} ions/cm^2. It should be noted that both the gas permeance and selectivity in the irradiated asymmetric membrane were enhanced when compared with those of the virgin asymmetric membrane. The mean projected range of the He ions in the membrane is 975 nm, indicating that the asymmetric membrane consisted of two-layer surfaces, the virgin polyimide and carbonized layers. The gas permeability through the two-layer surfaces was calculated using a simple resistance model.

$$\frac{L}{P} = \frac{L_P}{P_P} + \frac{L_C}{P_C} \tag{3a}$$

$$L = L_P + L_C \tag{3b}$$

where P, P_P, and P_C are the total gas permeability coefficient, the gas permeability coefficient through the virgin polyimide layer, and the gas permeability coefficient through the carbonized layer, respectively. L_P and L_C, which were the apparent thicknesses of the virgin polyimide and carbonized layers, were 2905 and 975 nm, respectively. Generally, the O_2 permeability through the polymer membrane does not depend on the O_2 pressure and was constant. Therefore, P_C values calculated from the O_2 permeability provide the accurate data. On the other hand, we could not determine P_C values from the CO_2 permeability, because the CO_2 permeability in the polyimide membrane obeyed the dual transport model as reported in the glass polymer membranes and showed the CO_2 pressure dependence.[25] The O_2 permeability coefficients and (O_2/N_2) selectivities of the irradiated asymmetric polyimide membrane are shown in Table 4. Both the permeability and selectivity of the carbonized layer calculated using the simple resistance model were significantly enhanced when compared with those determined for the virgin polyimide. Additionally, it is interesting to note that the (O_2/N_2) selectivity of the carbonized layer indicated higher values than those in the asymmetric membranes with a 80 nm thickness irradiated by a 50 keV He^+ with 3×10^{15} ions/cm^2. These findings mean that the ion depth in the skin layer has a significant influence on the gas permeability and selectivity of the irradiated asymmetric membranes and that controlling of the ion-irradiated layer is one of the important fabrication technologies for the development of a novel gas separation membrane.

Our greatest interest was the deposited energy effects of ion on the carbonized skin layer, which dominate the gas permeation properties. The ion-beam reactions induced in the polyimides are known to be sensitive to nuclear energy loss.[25,26] Figure 5 shows the profile of the nuclear energy loss vs the ion depth in the polyimide membrane calculated using a Monte Carlo simulation method, indicating that the energy loss strongly depends on the depth. Therefore, we consider that the polyimide structure in the ion-irradiated surface layer would be closely correlated to the amount of energy loss produced by unclear stopping and that the structure eventually determines the free volume and the free volume distribution formed in the membrane. The results in Table 3 really show the influence of the nuclear energy loss. In future research, we will elucidate the effects of the deposited energy such as the unclear energy loss on the polyimide structure and the gas permeation property.

Conclusions

The above studies have led to some interesting conclusions for the gas permeance and selectivity of the ion-irradiated asymmetric polyimide membranes. The gas permeances for the membrane showed an increase at a low ion fluence and a decrease at a high ion fluence. On the other hand, the gas selectivity increased with an increase in the ion fluence. One possibility may be that the gas permeation space, which can provide a high degree of size and shape discrimination between the gas molecules, was formed on the ion-irradiated skin surface and suppressed the permeability of N_2 and CH_4 rather than that of O_2 and CO_2.

Another interesting conclusion is that the thickness of the ion-irradiated skin layer had a significant influence on the gas permeability and selectivity. The polyimide structure in the ion-irradiated surface layer would be closely correlated to the amount of ion energy loss so that the structure may determine the free volume and the free volume distribution formed in the membrane.

It is desirable to prepare a polymer membrane with both a high gas permeability and selectivity for gas separation. The ion-irradiated asymmetric polyimide membrane prepared in this study showed interesting gas permeation results, and we consider that the ion irradiation would be one of the important membrane fabrication techniques for realizing a high gas permeability and selectivity.

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