1 Atmospheric-Pressure Plasma-Enhanced Chemical Vapor Deposition of Microporous Silica Membranes
2 for Gas Separation

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13 Abstract

14 Microporous silica membranes with high permselectivity are fabricated by atmospheric-pressure
15 plasma-enhanced chemical vapor deposition (AP-PECVD) using hexamethyldisiloxane as the precursor
16 in plasma working gases of pure argon, and mixture of argon with oxygen or nitrogen. A silica membrane
17 grown using plasma composed of a mixture of argon and nitrogen displays highly efficient gas separation,
18 with selectivities for He/N₂ and He/SF₆ of 196 and 820, respectively, and He permeance of 1.1×10^{-7} mol
19 m⁻² s⁻¹ Pa⁻¹ at 50°C. Characterization of the membranes by FTIR and X-ray photoelectron spectroscopies
20 reveals a relatively high concentration of carbon remains in the membrane grown using a mixture of
21 argon and nitrogen. Annealing at elevated temperature after plasma deposition improves the
22 permselectivity of the membranes. After annealing at 300°C, the permeance of He at 50°C increased to
23 4.0×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ with no marked decrease of selectivity (He/N₂ = 98, He/SF₆ = 770). The
24 annealed membrane also exhibits remarkable permselectivity for CO₂, showing selectivities for CO₂/N₂
25 and CO₂/CH₄ of 46 and 166, respectively, with CO₂ permeance of 1.9×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ at 50°C. AP-

PECVD shows great promise to fabricate microporous silica membranes highly permselective for gas separation.

1. Introduction

Amorphous silica membranes are a class of microporous inorganic membrane that has attracted great interest over the years. Amorphous silica membranes possess high stability towards a variety of chemicals and wide range of operating temperature, and exhibit the ability to separate small molecules from larger ones by molecular sieving through their microporous silica networks, thus showing high permselectivity.¹ Amorphous silica membranes prepared by chemical vapor deposition (CVD)^{2,3} or sol-gel methods⁴⁻⁶ are therefore promising candidates for use in harsh environments that conventional polymeric membranes cannot withstand. Furthermore, the tunable pore size of silica networks allows efficient separation with high permselectivity for a wide variety of applications, including H₂ and CO₂ separation.⁷⁻⁹

Recently, there has been growing interest in using plasma-assisted processes to fabricate microporous inorganic membranes.^{10,11} Compared with conventional CVD and sol-gel methods, plasma-assisted processes are preferable because of their low processing temperatures, which can be as low as room temperature. Several groups have fabricated microporous inorganic membranes using plasma-enhanced chemical vapor deposition (PECVD) under high vacuum. Roualdes et al. synthesized polysiloxane membranes using PECVD with organosilicon precursors such as hexamethyldisiloxane (HMDSO).¹² Kafrouni and his colleagues fabricated silicon carbonitride membranes using hexamethyldisilazane and ammonia as precursors.¹³ Ngamou et al. prepared a hybrid organically bridged silica membrane using 1,2-bis(triethoxysilyl)ethane as a precursor, and evaluated its pervaporation performance.¹⁴ Previously, we fabricated organosilica membranes via a two-step PECVD technique at low temperature that involved treatment with an HMDSO/Ar plasma followed by an HMDSO/O₂ plasma.^{15,16} The membranes prepared via 2-step PECVD exhibited excellent molecular sieving properties and possessed high stability against the exposure to steam at 300°C.¹⁵ Moreover, we reported that the

permselectivity of PECVD-derived silica membranes was controlled by the chemical structure of the precursors.¹⁷ However, the vacuum chamber systems used in PECVD are costly and unsuitable for large-scale membrane fabrication. Another issue is that the permeances of membranes grown by PECVD reported in previous studies are rather low compared with those of membranes obtained by conventional CVD or sol-gel technique.

Plasma deposition at atmospheric pressure is more versatile than that under vacuum. Importantly, because no vacuum systems are needed, plasma deposition at atmospheric pressure can be used to fabricate thin films in a continuous process, and thus can prepare membranes with a large area. One option to prepare inorganic membranes via plasma-based route at atmospheric pressure is the atmospheric plasma spraying technique, which uses a high-temperature plasma jet with typical temperatures of the order of 10,000 K.^{18, 19} In the atmospheric plasma spraying technique, ceramic and metal particles are fed into and melted in the high-temperature plasma jet, and then precipitated on a substrate to form a solid alloy or ceramic coating. Tung et al. prepared ceramic-metallic microfiltration membranes with a pore size of 0.2-0.4 μm using $\alpha\text{-Al}_2\text{O}_3$ particles with Ni and Cr as metal binders.¹⁸ They also synthesized photocatalytic TiO_2 membranes with a pore size of 0.35 μm that could be used to treat water through photodegradation of organisms and proteins under UV irradiation.¹⁹ An attempt to use high-temperature plasma to prepare gas separation membranes was performed by Chen and coworkers.²⁰ They modified poly(dimethylsiloxane) membranes using high-temperature plasma to form a permselective SiO_x layer on the membrane surface.²⁰ Such high-temperature plasma techniques are suitable to fabricate fully inorganic membranes but cannot be used to produce organic-inorganic hybrid membranes.

Another technique that has received considerable attention in recent years is atmospheric-pressure plasma-enhanced chemical vapor deposition (AP-PECVD), which uses non-equilibrium atmospheric-pressure plasma.²¹ Non-equilibrium plasma has an electron temperature much higher than those of ions and neutral species such as atoms and molecules. In this type of plasma, reactive species such as ions, radicals, and excited molecules can be produced at low temperature, even at room temperature, via

dissociation of gaseous molecules through collisions with plasma electrons. These reactive species can induce film-forming reactions both in the gas phase and on the growing film surface. Because of the low temperature of non-equilibrium plasmas, they can greatly lower the processing temperature compared with that using thermal plasma, and thus can minimize the thermal damage to the substrate.^{22,23} Therefore, AP-PECVD has emerged as a reliable technique to deposit functional thin films on a wide variety of substrates including thermal sensitive materials. As a result, AP-PECVD shows potential to prepare thin films such as dense silica coatings for surface protection layers on plastics,²⁴ amorphous silicon nitride thin films for anti-reflective coatings on solar cells,²⁵ and titanium nitride films for electronic devices.²⁶ The use of AP-PECVD to fabricate membranes for separation of gas and liquid phases has never been reported, and remains to be explored.

In the present study, we report the synthesis of supported microporous silica membranes for gas separation via AP-PECVD. Silica thin layer are deposited onto nanoporous substrates in a remote plasma of either pure argon or a mixture of argon with oxygen or nitrogen using HMDSO as a silica precursor. The effect of plasma working gas composition on the gas permeation properties of the membranes is investigated together with the physical and chemical characterization of the AP-PECVD-derived thin layers by Fourier transform infrared (FTIR) spectroscopy, X-ray photo electron spectroscopy (XPS), and scanning electron microscopy (SEM).

2. Experimental

2.1. Atmospheric-Pressure Plasma Deposition System

A schematic diagram of the AP-PECVD system is shown in **Figure 1**. The system consisted of gas and precursor feed lines, an atmospheric plasma source, and a deposition chamber with a diameter of 100 mm. A damage-free plasma jet (Plasma Concept Tokyo, Inc., Japan), which is a specific type of dielectric barrier discharge plasma jet,²⁷ was used as the plasma source. The atmospheric plasma was driven by a sinusoidal voltage with a maximum value of 6.0 kV at a frequency of 50 kHz. The plasma working gas was fed through the plasma source at a flow rate of 5.0 L min⁻¹ to form reactive species, and

was injected from a nozzle with a diameter of 1 mm into the center of the deposition chamber. Pure Ar or a mixture of Ar with O₂ (5.0 vol%) or N₂ (0.25 – 10.0 vol%) were used as the plasma working gas. The silicon precursor HMDSO was fed into the afterglow region of the plasma from the injection channel located 2 mm downstream of the nozzle exit by bubbling a flow of Ar as a carrier gas through the HMDSO liquid reservoir at 40 °C, which corresponds to a HMDSO/carrier gas molar ratio of 1:10. The flow rate of the Ar carrier gas was maintained at 200 mL min⁻¹. The substrate was placed at the center of the deposition chamber. The distance from the nozzle exit to the substrate was 5 mm. The atmosphere in the chamber was prevented from contamination by the surrounding atmosphere by an Ar gas curtain with a flow rate of 5.0 L min⁻¹. All deposition experiments were conducted at room temperature.

Figure 1. Schematic illustration of the AP-PECVD membrane fabrication system.

2.2. Film Characterization

The chemical structure of the films were analyzed by using FTIR (JASCO, FTIR-4100) and XPS (Thermo Fisher Scientific, ESCALAB 250Xi, Al-K α = 1486.6 eV). The films were deposited on silicon wafers and aluminum plates for FTIR and XPS analysis, respectively. The surface morphologies of the films deposited on silicon wafers and nanoporous substrates were observed by FE-SEM (Hitachi, S5000).

2.3. Membrane Fabrication and Gas Permeation Measurement

A porous α -alumina capillary tube (average pore size, 150 nm; outer diameter, 3 mm; length, 50 mm; kindly supplied by NOK, Co.) was used as a supporting substrate. Prior to the plasma deposition of organosilica layers, intermediate layers were prepared on the porous α -alumina substrates via a sol-gel method as reported previously.¹⁶ Briefly, a TiO_2 sol (0.72 wt%) was coated on the outer surface of a porous support, and the support was fired at 550 °C for 15 min to form a TiO_2 intermediate layer. SiO_2 - ZrO_2 sol (0.5 wt %; Si/Zr molar ratio = 1:1) was then coated on the TiO_2 intermediate layer and fired at 550 °C to form a SiO_2 - ZrO_2 intermediate layer. The pore size distributions of the intermediate layers were evaluated by nanoporimetry.²⁸ The average pore size of the substrates with a SiO_2 - ZrO_2 intermediate layer, which was defined at 50% of dimensionless permeability, was approximately 1 nm. Silica layers were then deposited on the intermediate layers by AP-PECVD. Because the substrates were tubular, they were rotated at 200 rpm and moved toward the axial direction at a rate of 1 mm min⁻¹ to ensure that the silica layer could uniformly deposit on the substrate surface.

To evaluate the gas permeation properties of the membranes fabricated by AP-PECVD, the gas permeances for He, H₂, CO₂, N₂, CH₄, and SF₆ were evaluated using the constant-volume variable-pressure method.¹⁷ The detail is shown in the Supporting Information (ESI-1†).

3. Results and discussion

Silica membranes were deposited using a remote plasma at atmospheric pressure consisting of either pure argon or a mixture of argon with oxygen or nitrogen. HMDSO was selected as the silica precursor, and fed into the afterglow region of the atmospheric-pressure plasma. Charged species such as ions and electrons decay rapidly in the afterglow because of their short mean free path at atmospheric pressure, so that the deposition is driven by neutral species such as excited molecules, atoms and radicals.

In the proposed AP-PECVD route, the HMDSO molecules injected in the afterglow region are first activated by reactions with excited argon atoms and/or reactive species of oxygen or nitrogen. The activated intermediates then react in the gas phase and/or on the substrate surface to form a silica thin layer.

To investigate the effect of plasma working gas composition on the structure and properties of the films produced, the chemical structure of the films deposited with different plasma working gases was characterized by FTIR spectroscopy and XPS. **Figures 2 and 3** show the FTIR spectra and survey XPS scans, respectively, of films deposited by AP-PECVD using pure Ar or a mixture of Ar with 5.0 vol% of O₂ or N₂ as the working gas. Plasma deposition using pure Ar was performed for 60 min, while that using O₂/Ar and N₂/Ar plasmas was conducted for 5 min considering the different deposition rate, which will be discussed later. The FTIR spectrum of the film deposited using pure Ar as the working gas (Figure 2a) contains the typical absorption bands of a SiO₂-like film. The strong absorption band at 1078 cm⁻¹ is attributed to the asymmetric stretching vibration of Si-O-Si bonds.²⁹ The absorption band at 930 cm⁻¹ originates from the bending vibration of Si-OH groups,²⁹ and the broad band at 3400 cm⁻¹ corresponds to the OH stretching of hydrogen-bonded OH groups.³⁰ The atomic composition of this film determined from the XPS data (Figure 3a) is summarized in **Table 1**. The atomic ratio of O/Si is 1.98, which is higher than that of the precursor HMDSO (O/Si = 0.5) and close to that stoichiometric SiO₂. The C/Si atomic ratio of 0.11 is considerably lower than that of HMDSO (C/Si = 3.0). These results indicate that the film deposited using pure Ar as the working gas has a SiO₂-like structure with a low content of carbon atoms.

Figure 2. FTIR spectra of silica films prepared using a) pure Ar, b) O₂/Ar (5.0 vol%), and c) N₂/Ar (5.0 vol%) as plasma working gas.

Figure 3. Survey XPS scans of silica films prepared using a) pure Ar, b) O₂/Ar (5.0 vol%), and c) N₂/Ar (5.0 vol%) as plasma working gas.

Table 1. Elemental composition of films fabricated by AP-PECVD with different working gases.

Working component	gas	Elemental composition [at.%]				Elemental ratio [-]	
		Si 2p	C 1s	O 1s	N 1s	C/Si	O/Si
Pure Ar		32.3	3.6	64.1	-	0.11	1.98
O ₂ /Ar (5.0 vol%)		31.9	3.2	64.9	-	0.10	2.04
N ₂ /Ar (5.0 vol%)		29.3	20.2	46.0	4.5	0.69	1.57

The film deposited using O₂/Ar as the working gas shows a similar FTIR spectrum to that of the film deposited using pure Ar but with an increased signal intensity of SiOH groups at 930 cm⁻¹, as illustrated in Figure 2b. The O/Si ratio determined from the XPS data (Figure 3b) is 2.04. These results indicate that the film deposited using O₂/Ar as working gas has a SiO₂-like structure with a OH-terminated surface which is formed by the attack of oxygen-related reactive species in the afterglow. In contrast, for the film deposited using N₂/Ar as the working gas, the FTIR spectrum clearly indicates the presence of organic functional groups (Figure 2c). The FTIR spectrum of this film displays characteristic absorption bands related to Si-(CH₃)_x groups: symmetric Si-(CH₃)_x stretching at 1260 cm⁻¹ and stretching of the saturated C-H bonds at around 3000-2800 cm⁻¹.³⁰ Meanwhile, the intensity of the peak corresponding to Si-OH at 930⁻¹ decreased, and that of the peak originating from Si-C at 800 cm⁻¹ increased. Moreover, the peak position of the Si-O-Si stretching vibration mode shifted to a lower wavenumber of 1053 cm⁻¹, which has been reported to be caused by the higher carbon content of a film.³¹ The atomic ratios of O/Si and C/Si in the film deposited using N₂/Ar as the working gas determined from the XPS analysis (Figure 3c) are 1.57 and 0.69, respectively. The results indicate that the film fabricated by AP-PECVD contain a larger organic content when N₂ is added to the working gas. The bands that can be attributed to amine, amide and/or oxime groups are also found at around 1750-1550 cm⁻¹ in the FTIR spectrum of the film deposited using N₂/Ar as the working gas, and the XPS analysis contains a signal at

399 eV corresponding to N 1s, suggesting the incorporation of nitrogen into the film during plasma deposition.³²

The effect of plasma working gas composition on the film deposition rate was investigated using the time dependence of FTIR spectra. **Figure 4a** shows the FTIR spectra from 1300 to 950 cm^{-1} of films deposited using a mixture of Ar with 5.0 vol% of N_2 as the working gas. It is apparent that the absorbance peak intensities of Si-O-Si stretching at around 1070 cm^{-1} in the film increases as the deposition time extended. The absorbance intensities of Si-O-Si stretching represent the mean thickness of plasma deposited layers. Thus, this increase of absorbance indicates that the deposition amount of the films increases the increasing deposition time. Figure 4b depicts the peak area of Si-O-Si stretching as a function of plasma deposition time for films deposited by AP-PECVD using different plasma working gases. In all cases, the peak area increases linearly with plasma deposition time, which indicates that the film thickness increases linearly over time. The gradient of the plot of peak area against deposition time, which represents the growth rate of the films, is markedly higher when a mixture of O_2/Ar or N_2/Ar is used as the working gas than when pure Ar is used. The gradients for the O_2/Ar and N_2/Ar systems are 39 and 28 times greater, respectively, than that for the pure Ar system. The considerable increase of growth rate with the addition of O_2 or N_2 to the plasma working gas indicates that the reactions with oxygen- or nitrogen-related reactive species in the afterglow play a dominant role in plasma deposition.

Figure 4. a) FTIR spectra of silica films prepared using N₂/Ar (5.0 vol%) as the plasma working gas with different deposition time. b) Peak area of the siloxane asymmetric vibration band of AP-PECVD-derived films prepared using different plasma working gases as a function of deposition time.

The effect of plasma working gas composition on the surface morphology of the deposited films was investigated by SEM. The deposition time was the same as that for FTIR and XPS samples. A granular structure with some small embedded particles is observed for the films grown with pure Ar and O₂/Ar as the working gas (Figure 5a and b, respectively). The film deposited using O₂/Ar plasma contains a number of cracks. The surface morphology of the film changes considerably when N₂ is added to the working gas mixture (Figure 5c), even though the deposition rate is similar to that using O₂/Ar. The film deposited using N₂/Ar as the working gas consists of nanosized-grains with extensive neck structure, showing a continuous crack-free coating.

Figure 5. Surface SEM images of AP-PECVD-derived silica films prepared with different working gases of (a) pure Ar, (b) O₂/Ar (5.0 vol%), and (c) N₂/Ar (5.0 vol%).

In this AP-PECVD system, the precursor fed to the afterglow region will be activated by excited atoms and/or molecules to form intermediate species for film formation. The above observations imply that the reaction between HMDSO and reactive species in the afterglow led to the formation of films with structures that depended on the plasma working gas composition. In the afterglow of pure Ar plasma, HMDSO will be dissociated by Ar metastables into gaseous intermediates, which will subsequently undergo a film forming step.³³ Possible dissociation pathways proposed in the literature consider the cleavage of both S-O and Si-C bonds in the precursor molecules.³⁴ Intermediate species such as (CH₃)₃-Si-O and (CH₃)₃-Si radicals could be formed through the dissociation of Si-O bonds, and other species such as (CH₃)₃-Si-O-Si-(CH₃)₂ radicals could be formed from the dissociation of Si-C bonds.³⁴ The recombination of such radicals through dangling bonds will consequently result in film formation on a substrate. Furthermore, because the C/Si atomic ratio of the film prepared with pure Ar (Figure 3a) is rather low compared with that of the above-mentioned radicals, an additional reaction that lowers the C/Si atomic ratio by removing carbon-containing functional groups, like abstraction of Si-(CH₃)₃ and CH₃ groups by some gaseous species, should also be considered. Reactions involving Si-CH₂ fragments and free H atoms resulting from the dissociation of CH conds could also occur; for example, the rearrangement of Si-CH₂ fragments to Si-CH₂-Si,³⁵ the formation of Si-H bonds,³⁶ and demethylation by free H atoms.³⁷ In the O₂/Ar system, ground-state O atoms, metastable O₂ molecules, and ozone are proposed to be the major reactive species in the afterglow,³⁸ which increase both the deposition rate and

O/Si ratio of the films. A possible oxidized intermediate originating from the reaction of HMDSO with oxygen-related species is a molecule with a silanon (Si=O) group, which can be further rearranged into a molecule with a silanol (Si-OH) group.³⁹ Because two silanol groups can react to form a siloxane (Si-O-Si) structure, this reaction route, as well as direct reaction of oxygen-related species with the film surface, might be responsible for the formation of a silica-like structure with Si-OH-terminated structure, as described in Figure 2b. For the N₂/Ar system, ground state N atoms and metastable N₂ molecules are regarded as the major reactive species in the afterglow of atmospheric-pressure nitrogen plasmas.⁴⁰ Although the reaction of HMDSO in nitrogen plasma is not fully understood, it is postulated that nitrogen-related species can facilitate the deposition process. Analogously to the reaction of hexamethyldisilazane in nitrogen plasma,^{25,32} incorporation of nitrogen into the film (confirmed in Figures 2c and 3c), could occur via recombination of NH radicals with intermediates from HMDSO.

Silica membranes were deposited by AP-PECVD onto porous α -alumina substrates with a nanoporous silica–zirconia intermediate layer prepared by sol-gel processing to investigate their gas permeation properties. Silica thin layers were prepared using either pure Ar or a mixture of Ar containing 5.0 vol% O₂ or N₂ as the plasma working gas. **Figure 6** shows a cross-sectional SEM image of a silica membrane deposited by AP-PECVD using a 0.25 vol% N₂/Ar mixture as the plasma working gas with a total deposition time of 20 min. The membrane has an asymmetric structure with a thin silica top layer with no visible cracks or defects, and is completely covered the nanoporous substrate surface.

Figure 6. Cross-sectional SEM image of a membrane deposited by AP-PECVD using a N₂/Ar (0.25 vol%) as the plasma working gas with total deposition time of 20 min.

Gas permeances of the membranes were evaluated with He (kinetic diameter, $d_i = 0.26$ nm), H₂ (0.289 nm), CO₂ (0.33 nm), N₂ (0.364 nm), CH₄ (0.38 nm), and SF₆ (0.55 nm). **Figure 7** shows gas permeances at 50 °C for the silica membranes fabricated by AP-PECVD as a function of the kinetic diameter of the permeating molecules. Considering the difference in the rate of deposition between different plasma working gases, the total deposition time was 20 min for the membrane prepared using pure Ar plasma, while that of the membranes deposited using either O₂/Ar or N₂/Ar plasma was 3 min, in order to obtain similar permeance of He. After plasma deposition, the gas permeances decreased by two orders of magnitude from that of a substrate with a nanoporous silica–zirconia intermediate layer (N₂ permeance of 3×10^{-6} mol m⁻² s⁻¹ Pa⁻¹). Of the three types of membranes, only the membrane prepared using N₂/Ar as the plasma working gas shows selectivity that is much higher than ideal Knudsen selectivity. The membrane fabricated using N₂/Ar plasma exhibits permeance ratios of He/H₂, He/N₂, and He/SF₆ of 1.6, 29.9, and 68.8, respectively, with a He permeance of 0.52×10^{-7} mol m⁻² s⁻¹ Pa⁻¹. Gas permeances decrease with increasing kinetic diameter of the gases, indicating the membrane has a microporous structure with molecular sieving properties. Surprisingly, compared with silica membranes prepared via PECVD under vacuum, which showed He permeances in the range of 10^{-9} – 10^{-8} mol m⁻² s⁻¹

Pa⁻¹, the membrane prepared using AP-PECVD with N₂/Ar plasma displays permeance that is at least one order of magnitude higher but similar molecular sieving properties.^{15-17,41} These results demonstrate that AP-PECVD can fabricate microporous silica thin layer with molecular sieving properties.

Figure 7. Single gas permeances at 50 °C of membranes prepared by AP-PECVD with different working gases as a function of kinetic diameter of the permeating molecules.

The membrane prepared using pure Ar as the plasma working gas shows higher permeances than those of the membrane prepared with N₂/Ar plasma, for example, He permeance of $1.51 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, but their selectivity does not exceed the Knudsen selectivity. This is probably caused by the low deposition rate of the membrane prepared using pure Ar, which makes it difficult to cover the whole substrate surface within a reasonable deposition period. The membrane prepared using O₂/Ar as the plasma working gas exhibits He permeance similar to that of the membrane fabricated with N₂/Ar plasma because of their similar deposition rates, as discussed in Figure 4b. However, the selectivity of this

membrane is rather low, almost the same as the Knudsen selectivity, which is probably caused by the defects in the deposited layer that were observed by surface SEM (Figure 5b). The permeance ratio of He/H₂ for the membrane fabricated using O₂/Ar as the plasma working gas is 1.3, which did not agree with the predications of the Knudsen mechanism (0.71), indicating that the selectivity for this gas pair is not determined based on their weight, but on their size. This suggests that small pores also exist in the O₂/Ar plasma-derived top-layer, through which only small gases can permeate. A similar bimodal porous structure was also reported for a silica membrane prepared by conventional PECVD using HMDSO and O₂ plasma under vacuum.¹⁶

To further improve the gas permselectivity of AP-PECVD-derived silica membranes, the effect of N₂ concentration in the plasma working gas was investigated. **Figure 8a-c** displays surface SEM images of films deposited by AP-PECVD on Si substrates using N₂/Ar with different N₂ concentrations as the plasma working gas with 5 min of deposition time. The surface morphology of the films depends on the N₂ concentration of the working gas. The size of nanoscale grains in the film increases with the N₂ concentration of the working gas. The film deposited using a N₂ concentration of 0.25 vol% consists mostly of nanograins finer than 100 nm and has uniform structure (Figure 8a), while that fabricated using 5.0 vol% N₂ consists of nanograins with a diameter of approximately 500 nm (Figure 8c). **Figure 9** shows the growth rate defined as the absorption peak area of the Si-O-Si stretching vibration at 1078 cm⁻¹ as a function of N₂ concentration in the plasma working gas. The peak area growth rate increases with N₂ concentration between 0 and 5.0 vol%, but becomes constant at higher N₂ concentration. The deposition rate at a N₂ concentration of 0.25 mol% is 10-fold lower than that at a N₂ concentration of 5.0 mol%. The enhanced deposition rate at higher N₂ concentration can be ascribed to the increased concentration of nitrogen-related reactive species in the afterglow, which helps to enhance the dissociation of HMDSO to give film-forming intermediates.

Figure 8. Surface SEM images of AP-PECVD-derived silica films prepared using the plasma working gas with different N_2 concentrations of a) 0.25 vol%, b) 1.0 vol%, and c) 5.0 vol%.

Figure 9. Effect of N_2 concentration in the plasma working gas on the deposition rate of films deposited on silicon wafer.

Figure 10 shows gas permeances at 50 °C for membranes prepared by AP-PECVD using N_2/Ar plasma with different N_2 concentrations as a function of kinetic diameter of the permeating molecules. The total deposition time for the membranes prepared using 0, 0.25, and 5.0 vol% N_2/Ar were 20, 10, and

3 min, respectively, in order to compare the performance of these membranes with similar He permeances. The gas permselectivity of these membranes is greatly improved by lowering the N₂ concentration in the working gas to 0.25 vol%. The membrane prepared using 0.25 vol% N₂/Ar as the working gas with a deposition time of 10 min shows a high He permeance of $1.1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ with permeance ratios of He/N₂ and He/SF₆ of 196 and 820, respectively. Both the He permeance and permeance ratios are higher than those of the membrane prepared using 5.0 vol% N₂/Ar as a working gas. These results suggest that deposition of a silica layer using a low N₂ concentration of 0.25 vol% is preferable for membrane fabrication probably because the rate of the gas-phase reaction and the rate of the surface reaction are balanced. Although further investigation would be needed in the future with gas permeation at different temperatures in order to discuss the permeation mechanism in detail, the high permselectivity as shown in Figure 10 presents the great promise of AP-PECVD-derived silica membranes in molecular separation applications.

Figure 10. Single gas permeances at 50 °C for membranes prepared by AP-PECVD with different N₂ concentrations as a function of kinetic diameter of the permeating molecules.

Finally, we investigated how annealing a membrane at elevated temperature after plasma deposition affected its properties. A membrane prepared using 0.25 vol% N₂/Ar as the working gas was annealed at 300 °C in inert atmosphere for 60 min. This annealing step can help to remove physically adsorbed organosilicon monomer and water, which may block the permeation pathway and decrease the membrane performance, from the plasma-deposited layer, and can also rearrange the structure of the plasma-deposited layer by thermally induced reactions. **Figure 11** and b display the FTIR spectra of films fabricated by AP-PECVD before and after annealing at 300 °C. For the annealed film, the absorption band attributed to Si-O-Si stretching at 1078 cm⁻¹ has the same intensity as that of the as-deposited film. The peak at 1260 cm⁻¹ originating from Si-(CH₃)_x bending is also unchanged after annealing. In contrast, the intensities of the absorption bands corresponding to Si-OH and OH stretching at 930 and 3400 cm⁻¹, respectively, decreased after annealing. This decrease in intensities of Si-OH and OH peaks suggests that thermal treatment causes the condensation of silanol groups resulting in the formation of siloxane group. The decrease in OH peak intensity also suggests the release of adsorbed water from the AP-PECVD-derived layer.

Figure 11. FTIR spectra of AP-PECVD-derived silica films a) before and b) after the thermal annealing at 300°C under vacuum.

Interestingly, as shown in **Figure 12**, the thermally annealed membrane shows an improved He permeance of $4.0 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ compared with that of the as-deposited membrane, due to the removal of physically adsorbed compounds in the plasma-deposited layer. Even though the He permeance increases by 3.6 times, the membrane maintains selectivities for He/N₂ and He/SF₆ of 98 and 770, respectively, indicating high thermal stability of the plasma-deposited layer. Furthermore, the membrane also exhibits remarkable permselectivity for CO₂, with permeance ratios for CO₂/N₂ and CO₂/CH₄ of 46 and 166, respectively, and CO₂ permeance of $1.9 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 50 °C. Currently, DDR⁴² and SAPO-34⁴³ zeolite membranes are reported to be the most effective microporous inorganic membranes developed for CO₂ separation from CO₂/CH₄ mixtures. As summarized in **Table 2**, the membranes fabricated by AP-PECVD have high CO₂ permeance and selectivity that is comparable with that of zeolite membranes. The high CO₂/N₂ and CO₂/CH₄ permeance ratios of the membranes after thermal annealing

can be ascribed to the molecular sieving behavior of the AP-PECVD-derived silica layer with a suitable pore size for CO₂ permeation. CO₂ separation of AP-PECVD-derived silica membranes will be further investigated with a binary mixture in the future work.

Figure 12. Single gas permeances at 50 °C of membranes before and after the thermal annealing at 300°C under vacuum as a function of kinetic diameter of the permeating molecules.

Table 2. CO₂/CH₄ separation properties through inorganic membranes.

Membrane	<i>T</i> [°C]	CO ₂ permeance [10 ⁻⁷ mol m ⁻² s ⁻¹ Pa ⁻¹]	CO ₂ /CH ₄ selectivity [-]	Ref.
AP-PECVD silica	50	1.9	166 ^{a)}	This work
DDR zeolite	28	7	220 ^{b)}	[42]
SAPO-34	22	18	171 ^{b)}	[43]

^{a)}Ideal selectivity; ^{b)} selectivity for a CO₂/CH₄ mixture (50:50).

Conclusions

Microporous silica membranes for gas separation were synthesized via AP-PECVD. The membrane deposited in the afterglow of N₂/Ar mixtures exhibited molecular sieving properties, while those prepared in either pure Ar or O₂/Ar afterglow showed Knudsen-like selectivity. By optimizing N₂ concentration in the plasma working gas, a high He permeance of $1.1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ with He/N₂ and He/SF₆ selectivities of 98 and 820, respectively, at 50 °C were achieved for the membrane deposited using 0.25 vol% N₂/Ar. Annealing the membranes at elevated temperature after plasma deposition can further improve their permselectivity. The membrane annealed at 300 °C showed highly efficient gas separation performance. The selectivities for He/N₂ and He/SF₆ of the annealed membrane were as high as 98.5 and 771, respectively, with He permeance of $4.0 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 50 °C. This membrane also exhibited remarkable permselectivity for CO₂ comparable with that of zeolite membranes; its selectivities for CO₂/N₂ and CO₂/CH₄ were 46 and 166, respectively, with CO₂ permeance of $1.9 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 50 °C. These results reveal the great promise of AP-PECVD as a novel technique to fabricate microporous silica membranes for separation applications.

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Graphical abstract