Preparation and characterization of DLC/SiO₂/Al₂O₃ nanofiltration membrane

JIN-SU JEONG¹, CHURL-HEE CHO[†], JONG-OH KIM[‡], DONG-HUN YEO[#]
and WON-YOUL CHOI^{1,*}

¹Department of Metal and Materials Engineering, Gangneung-Wonju National University, Gangneung 210 702, Korea

[†]Graduate School of Green Energy Technology, Chungnam National University, Daejeon 305 764, Korea

[‡]Department of Civil Engineering, Gangneung-Wonju National University, Gangneung 210 702, Korea

[#]Advanced Materials Convergence Division, Korea Institute of Ceramic Engineering and Technology, Seoul 153 801, Korea

MS received 12 July 2012; revised 27 September 2012

Abstract. High quality ceramic thin films were fabricated by thin film deposition process in semiconductor field in order to fabricate high performance carbon/SiO₂/Al₂O₃ membrane. α -Al₂O₃ substrate was used as a supporting material. A severe thermal stress and rough surface for active ceramic top layer such as zeolite were observed. To overcome thermal stress, intermediate layer of SiO₂ and diamond-like carbon (DLC) thin films were used. SiO₂ and DLC thin films on porous alumina support were deposited using plasma-enhanced chemical vapour deposition (PECVD). Homogeneous and smooth surfaces and interfaces of DLC/SiO₂/Al₂O₃ membrane were observed by FESEM. The phases of DLC and SiO₂ thin films were identified by X-ray diffraction pattern. Gas permeabilities of the nanofiltration membrane with DLC/SiO₂/Al₂O₃ were observed at various annealing temperatures. Mixed gas permeability of the membrane with 1 μ m-thick SiO₂ and 2 μ m-thick DLC thin film annealed at 200 °C was ~ 18 cc/m at 1018 mb back pressure.

Keywords. Thin films; DLC/SiO₂/Al₂O₃ membrane; nanofiltration.

1. Introduction

Nanofiltration membranes can be generally classified into two major groups of organic–polymeric and inorganic–ceramic membranes. Polymeric membranes have been commercially available in a lot of different polymeric materials such as polysulfone, cellulose acetate and polyamide. They are relatively easy to prepare and can be produced cheaply at large scale. However, their chemical stability is limited with respect to corrosive media, like strong acids and organic solvents (Mulder 1996; Hestekin *et al* 1999). The application is also limited to moderate temperature due to its thermal instability. In recent days, much research is focused on ceramic nanofiltration membranes. Ceramic membranes generally show high thermal, chemical and mechanical stabilities. They are expected to constitute a promising alternative for polymeric membranes (Burggraaf and Cot 1996; Gestel *et al* 2002, 2006).

High performance ceramic nanofiltration membrane can only be obtained in an asymmetric multilayer structure. The multilayer structure consists of supporting materials, mesoporous intermediate layers and microporous top layer. Alumina, titania, zirconia and silica are considered as

the main supporting materials for the formation of multilayer structures (Vacassy *et al* 1997; Luyten *et al* 2000; Benito *et al* 2004, 2005). Their preparation starts with the production of high quality supporting materials, because the performance of ceramic nanofiltration membrane is greatly influenced by the structural properties of supporting materials (Luyten *et al* 1997, 1999). The modification of intermediate layers is also very important for the preparation of top layer. The modification of intermediate layers with fine-grained mesoporous ceramic thin film is necessary in order to reduce the coarse pore of the supporting materials and large surface irregularities or defects. The preparation process generally includes a heating process such as sol–gel, hydrothermal and annealing. The heating process makes a cracking and infiltration from the difference of thermal expansion coefficient of supporting materials and top layer. To prevent cracking and infiltration, thermal expansion of intermediate layers is also considered. Especially, in case of alumina as a supporting material and zeolite as a top layer, the difference of thermal expansion coefficient is very large and it makes some defects in ceramic nanofiltration membrane. Because, thermal expansion coefficient of alumina and zeolite are $8.5 \times 10^{-6} \text{ K}^{-1}$ and $2 \times 10^{-5} \text{ K}^{-1}$, respectively, the intermediate layer having middle value between alumina and zeolite is needed to

*Author for correspondence (cwyo@gwnu.ac.kr)

release thermal stress (Tschaufeser and Parker 1995; Bayuseno *et al* 1999).

To prevent cracking and infiltration resulting from thermal stress and shock in ceramic nanofiltration membranes, hydrogenated amorphous carbon (diamond-like carbon, DLC) of $2 \times 10^{-6} \text{ K}^{-1}$ and silicon dioxide (SiO_2) of $5 \times 10^{-7} \text{ K}^{-1}$ for intermediate layer have been used. DLC and SiO_2 thin films with various thickness were prepared by plasma-enhanced chemical vapour deposition (PECVD). These films were annealed at several temperatures. Microstructure and phase with annealing temperature were observed by field emission scanning electron microscopy (FESEM) and X-ray diffraction pattern (XRD). Gas permeability was measured and the composition of mixed gas was analysed by gas chromatography (GC).

2. Experimental

2.1 Support preparation

To fabricate the support of $\alpha\text{-Al}_2\text{O}_3$ for nanofiltration membrane, Al_2O_3 powder of 0.5 μm average diameter was used. Al_2O_3 powder was mixed with 2 wt% MC solution. The disk-type alumina support of 2 mm thickness and 3 cm diameter was sintered at 1200 $^\circ\text{C}$ for 1 h by typical solid-state reaction. Surface morphologies of macroporous Al_2O_3 support were observed by field emission scanning electron microscopy (FESEM, Philips XL 30SFEG).

2.2 Thin films preparation

To reduce the residual stress of SiO_2 thin film, low stress PECVD method was used. It is promising the low stress thin film by optimized plasma excitation frequency (Alayo *et al* 1998; Mackenzie *et al* 2005). The deposition temperature and RF power for SiO_2 thin film were controlled 350 $^\circ\text{C}$ and 275 W, respectively. Mass flows of SiH_4 , N_2O and N_2

source gases were 75, 3300 and 1200 sccm, respectively. To increase the thickness of SiO_2 thin film, the deposition time was increased and thickness of 1–4 μm was obtained. DLC thin film was also deposited by PECVD method and mass flow of source gas, CH_4 was 40 sccm in 10^{-5} torr vacuum chamber. The deposition temperature and RF power were 25 $^\circ\text{C}$ and 0.74 W, respectively. Low stress DLC thin film having 2 μm thickness was obtained for 3 h by PECVD. Figure 1 shows schematic view of the ceramic nanofiltration membrane of DLC/ SiO_2 / Al_2O_3 multilayer structure.

2.3 Characterization

Microstructure of surfaces and interfaces of DLC/ SiO_2 / Al_2O_3 membrane were observed by FESEM. The phases of DLC and SiO_2 thin film were identified by XRD. To analyse the gas permeability, single gas of He and mixed gas of 40% CO_2 and 60% N_2 were used. The ratio which is similar to the exhaust fumes of thermal power generator was selected. Gas permeabilities of the nanofiltration membrane with DLC/ SiO_2 / Al_2O_3 were observed at various annealing temperatures. Figure 2 shows diagram of the gas separation system.

3. Results and discussion

3.1 Support and intermediate layers

Supporting materials of Al_2O_3 powder was prepared and sintered by typical solid-state reaction. The disk-type Al_2O_3 support of 2 mm thickness and 3 cm diameter was fabricated. Figure 3(a) and (b) show top view and cross-sectional view of Al_2O_3 support, respectively. The average pore size from figure 3(a) was about 300 nm. This macroporous structure was uniformly observed in figure 3(b) and was adequate to the supporting materials of nanofiltration multilayer membrane.

DLC and SiO_2 thin films for multilayer nanofiltration membrane were deposited by PECVD. The nanofiltration membrane having 2 μm thick DLC/1 μm -thick SiO_2 / Al_2O_3

Figure 1. Schematic view of ceramic nanofiltration membrane of DLC/ SiO_2 / Al_2O_3 structures.

Figure 2. Diagram of gas separation system.

Figure 3. Microstructures of Al₂O₃ support by FESEM: (a) top view and (b) cross-sectional view.

structure was annealed at various temperatures of 200, 250 and 450 °C. The microstructure of nanofiltration membrane was observed by FESEM. Figure 4(a) and (b) show top view and cross-sectional view of nanofiltration membrane without annealing, respectively. As-deposited DLC thin film has a grain size of $\sim 5 \mu\text{m}$ and a very smooth surface morphology. The macrostructure of support was not observed due to microporous DLC thin film. To obtain the crystalline and more dense microstructure, DLC/SiO₂/Al₂O₃ nanofiltration membrane was annealed from 200–450 °C. Figure 4(c), (e) and (g) show top view of nanofiltration membrane at 200, 250 and 450 °C, respectively. Figure 4(d), (f) and (h) show the cross-sectional view of nanofiltration membrane at 200, 250 and 450 °C, respectively. The grain size of DLC thin film was decreased with annealing temperature. DLC thin film was mostly removed at 450 °C and the surface of SiO₂ thin film was shown in figure 4(g). The carbon in DLC thin film might be oxidized to carbon dioxide for annealing. Figure 5 shows energy dispersive X-ray spectroscopy (EDS) analysis data of figure 4(c). Carbon and silicon peaks were obtained from DLC and SiO₂ thin film of nanofiltration membrane. Similar EDS data was observed at higher annealing temperature. Figure 6 shows XRD patterns of DLC/SiO₂/Al₂O₃ nanofiltration membrane annealed at 450 °C. All peaks were from α -Al₂O₃ support. It revealed that DLC and SiO₂ thin films were amorphous. There is no evidence of grain growing and phase transitions resulting from the annealing process.

3.2 Gas permeability

The characterization of nanofiltration membrane was investigated by measuring the gas permeability and gas chromatography. To optimize the annealing temperature of DLC/SiO₂/Al₂O₃ nanofiltration membrane, gas permeability was observed on He single gas. Figure 7(a) shows gas permeability of nanofiltration membrane with 1 μm thick SiO₂ and 2 μm thick DLC on Al₂O₃ support with annealing temperature. The back pressure was 1018 mb on

He single gas at 70 °C. Gas flux for nanofiltration membrane without annealing showed a very high permeability of 52 ccm. Gas flux with annealing temperature was increased from 18–45 ccm. This increasing gas flux with annealing temperature resulted from the oxidation of DLC thin film with annealing process. This result corresponds to the microstructure of figure 4(c), (e) and (g). The oxidation of DLC thin film makes an easy He gas transfer through DLC/SiO₂/Al₂O₃ nanofiltration membrane.

To optimize the thickness of SiO₂ thin film, gas permeability was observed on He single gas at 70 °C. Figure 7(b) shows He gas permeability of 1, 2, 3 and 4 μm thick SiO₂ thin films annealed at 200 °C. He gas flux was increased from 18 to ~ 220 ccm with the thickness of SiO₂ thin film. Rough surface morphologies with increasing thickness of SiO₂ thin film was observed by FESEM. Microstructural quality of DLC thin film on SiO₂ thin film was affected by the surface of substrate, SiO₂. The high gas flux in 4 μm thick SiO₂ can be expressed with low-quality DLC thin film resulting from rough surface of SiO₂.

For application of thermal power plant, gas permeability was measured on mixed gas of 40% CO₂ and 60% N₂. Figures 8(a) and (b) show gas flux with annealing temperature and thickness of SiO₂ thin film, respectively. The influence of mixed gas flux with annealing temperature and thickness were similar to figure 7 of He single gas. The lowest gas flux of ~ 18 ccm was shown in 1 μm thick SiO₂ and 2 μm thick DLC on Al₂O₃ annealed at 200 °C. It reveals that proper annealing temperature and SiO₂ thickness for DLC/SiO₂/Al₂O₃ were 200 °C and 1 μm , respectively. The composition of mixed gas flux was analysed by gas chromatography (GC). Figure 9 shows GC data of mixed gas flux passing through 1 μm thick SiO₂/2 μm thick DLC/Al₂O₃ nanofiltration membrane. The flux obtained from the mixed gas of 40% CO₂ and 60% N₂ consisted of 13.64% CO₂ and 86.24% N₂, respectively. The content of CO₂ gas which has a large molecule size was decreased $\sim 26\%$ in mixed gas and CO₂ molecules were more difficult to pass through 1 μm thick SiO₂/2 μm thick DLC/

Figure 4. Microstructure of 1 μm thick SiO_2 /2 μm thick $\text{DLC}/\text{Al}_2\text{O}_3$ nanofiltration membrane at various annealing temperatures: (a) top view of membrane without annealing, (b) cross-sectional view of membrane without annealing, (c) top view of membrane annealed at 200 °C, (d) cross-sectional view of membrane annealed at 200 °C, (e) top view of membrane annealed at 250 °C, (f) cross-sectional view of membrane annealed at 250 °C, (g) top view of membrane annealed at 450 °C and (h) cross-sectional view of membrane annealed at 450 °C.

Figure 5. Energy dispersive X-ray spectroscopy (EDS) analysis data of figure 4(c).

Figure 6. XRD patterns of 1 μm thick SiO₂/2 μm thick DLC/Al₂O₃ nanofiltration membrane annealed at 450 $^{\circ}\text{C}$.

Al₂O₃ nanofiltration membrane than N₂ molecules. This nanofiltration property of 1 μm thick SiO₂/2 μm thick DLC/Al₂O₃ will be useful for thermal power plant and car exhaust fumes.

4. Conclusions

Nanofiltration membrane with DLC/SiO₂/Al₂O₃ multilayer structure was fabricated and characterized. Al₂O₃ support was sintered by solid-state reaction and DLC and SiO₂ thin films were deposited by PECVD. Gas permeability on annealing temperature and SiO₂ thickness was investigated. The optimum annealing temperature and SiO₂

Figure 7. Single gas (He) permeability of DLC/SiO₂/Al₂O₃ nanofiltration membrane (a) gas flux of nanofiltration membrane with 2 μm thick DLC/1 μm thick SiO₂/Al₂O₃ at various annealing temperatures and (b) gas flux of DLC/SiO₂/Al₂O₃ nanofiltration membrane at various thickness of SiO₂ thin films.

thickness were 200 $^{\circ}\text{C}$ and 1 μm , respectively. Gas permeability of mixed gas having 40% CO₂ and 60% N₂ was observed and the flux was 18 ccm at 1018 mb back pressure. The flux consists of 13.64% CO₂ and 86.24% N₂. It reveals that CO₂ molecules were more difficult to pass through 1 μm thick SiO₂/2 μm thick DLC/Al₂O₃ nanofiltration membrane than N₂ molecules. The nanofiltration properties of DLC/SiO₂/Al₂O₃ multilayer structure will be useful for thermal power plant and car exhaust fumes.

Figure 8. Mixed gas (40% CO₂ and 60% N₂) permeability of DLC/SiO₂/Al₂O₃ nanofiltration membrane: (a) gas flux of the nanofiltration membrane with 2 μm thick DLC/1 μm thick SiO₂/Al₂O₃ at various annealing temperatures and (b) gas flux of DLC/SiO₂/Al₂O₃ nanofiltration membrane at various thickness of SiO₂ thin films.

Acknowledgments

This research was financially supported by the Ministry of Education, Science Technology (MEST) and National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation (Grant No. 2012H1B8A2026009) and Korea CCS R&D Centre (KCRC) funded by MEST of Korea (Grant No. 2012-0008912).

Figure 9. Gas chromatography (GC) data of mixed gas flux passed through 1 μm thick SiO₂/2 μm thick DLC/Al₂O₃ nanofiltration membrane.

References

- Alayo M, Pereyra I and Carreno M 1998 *Thin Solid Films* **332** 40
- Bayuseno A, Latella A and O'Connor B 1999 *J. Am. Ceram. Soc.* **82** 819
- Benito J, Conesa A and Rodriguez M 2004 *Bol. Soc. Ceram.* **5** 821
- Benito J, Conesa A, Rubio F and Rodriguez M 2005 *J. Eur. Ceram. Soc.* **25** 1895
- Burggraaf A and Cot L 1996 *Fundamentals of inorganic membrane science and technology* (Amsterdam, Holland: Elsevier)
- Gestel T, Kruidhof H, Blank D and Bouwmeester H 2006 *J. Membr. Sci.* **284** 128
- Gestel T, Vandecasteele C, Buekenhoudt A, Dotremont C, Luyten J, Leysen R, Bruggen B and Maes G 2002 *J. Membr. Sci.* **207** 73
- Hestekin J, Smothers C, Bhattacharyya D, Ghorpade A and Hannah R 1999 *Nanofiltration for removal of organics from aqueous and organic solvent streams*, Dallas, TX, Presented at the 4th Topical conference on separations science & technology, membrane separation in food and pharmaceutical
- Luyten J, Coymans J, Smolders C, Vercauteren S, Vansant E and Leysen R 1997 *J. Eur. Ceram. Soc.* **17** 273
- Luyten J, Coymans J, Adriansen W and Leysen R 1999 *World ceramic congress on alternative process routes for better ceramic membrane supports*, Florence, Italy, Presented at the 9th CIMTEC
- Luyten J, Gestel T, Coymans J and Smolders C 2000 *Ceram. Trans.* **115**
- Mackenzie K, Johnson D, Devre M, Westerman R and Reelfs B 2005 *Electrochem. Soc. Proc.* **1** 148
- Mulder M 1996 *Basic principles of membrane technology*, (Dordrecht: Holland, Kluwer Academic) 2nd edn
- Tschaufeser P and Parker S 1995 *J. Phys. Chem.* **99** 10609
- Vacassy R, Guizard C, Thoraval V and Cot L 1997 *J. Membr. Sci.* **132** 109