

Plasma treatment of hydrophobic sub-layers to prepare uniform multi-layered films and high-performance gas separation membranes

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ABSTRACT

Uniform and defect-free silica films were prepared by spin-coating silica sols on plasma-treated hydrophobic sub-layers. Three kinds of silica films were prepared using tetraethoxysilane (TEOS), bis(triethoxysilyl)ethane (BTESE) and bis(triethoxysilyl)octane (BTESO) via sol-gel method. First, hydrophobic sub-layers were pre-coated on silicon wafers with Me-SiO₂ sols prepared from mixtures of methyltrimethoxysilane (MTMS) and TEOS. After firing at 400 °C, the films showed water contact angles of 120°. Then TEOS- and BTESE-derived sols were directly spin-coated on the Me-SiO₂ films, resulting in separated and scattered coatings. A H₂O/N₂ plasma modification method was used to change the properties of the Me-SiO₂ films from hydrophobicity to hydrophilicity without damaging either the surface morphology or the bulk chemistry. After the treatment, the TEOS- and BTESE-derived sols formed homogenous films. On the other hand, the Me-SiO₂ films were fully coated with BTESO either with or without plasma treatment. This was probably due to both the polar (–OH) and non-polar (long –CH₂) portions of the BTESO-derived sols. For gas separation applications, the corresponding BTESE membranes showed great improvement in gas selectivity after the plasma treatment of hydrophobic Me-SiO₂ layers.

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1. Introduction

Coating silica films or silica doped with other materials on various types of substrates has many applications that include optics, electronics, and corrosion protection [1–4]. Recently, silica materials on the application to porous membranes for molecular separation have drawn a great deal of attention [5]. One of the most important applications is gas separation such as H₂ purification, CO₂ capture or O₂ enrichment [6–8]. In general, porous silica membranes are prepared by coating silica sols on a hydrophilic intermediate layer (γ-alumina, SiO₂-ZrO₂ or TiO₂), followed by drying and calcination [6–10]. However, when water vapor is present in the separation processes, this can affect gas separation performance of membranes [11,12]. In our previous work, organosilica membranes showed excellent CO₂ separations under dry conditions, but CO₂ permeance was drastically decreased in the presence of water vapor due to adsorption and/or capillary condensation of water molecules in hydrophilic SiO₂-ZrO₂ intermediate layers [13]. Many hydrophobic and super-hydrophobic materials have been studied coating on silicon wafers or glass and obtained

water-repellent surface and self-cleaning properties [14,15]. Therefore, we propose the first attempt to coat microporous silica materials on the hydrophobic sub-layers, in order to obtain excellent performance for gas separation under humid conditions. The proposed asymmetric structures of porous membranes are shown in Fig. 1, which will avoid adsorption or condensation of water vapor.

Coated films do not demonstrate good performance unless the coatings are uniform and continuous without defects that include cracks, segregation, or scattered points on the substrates [16–19]. Polymer coatings have been widely investigated, for factors as diverse as different types of solvent, and the concentration and molecular weight of coating polymer [20–23]. The compatibility between solvent/polymer, polymer/substrate, and solvent/substrate plays an important role in the quality of coatings. Compared with other methods, plasma techniques show several advantages on improvement of coatings: shorter reaction times, lower temperature processes, overcoming the use of potentially toxic substances or solvents, and the grafting of a wider variety of functional groups. In addition, these films are generally free of pinholes, highly resistant to corrosion and very adhesive to substrates [24,25].

In this work, three kinds of silica sols, TEOS, BTESE, and BTESO, which have different organic groups tailoring the networks were deposited on hydrophilic and hydrophobic substrates by

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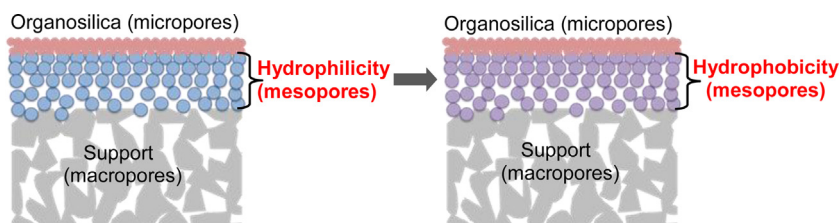


Fig. 1. Schematic structures of the porous membranes.

spin-coating. In addition, we propose the possibility of modifying the surface characteristics of Me-SiO₂ sub-layers from hydrophobic to hydrophilic without affecting the bulk properties by using H₂O/N₂ plasma treatment to form uniform and continuous films of top layers. Organosilica membranes coated on Me-SiO₂ layers with plasma treatment for gas separation were also discussed. This work offers a new strategy that can be used to fabricate multi-layered coating of hydrophilic and hydrophobic layers for gas separation membranes. As far as the authors know, few research groups have investigated silica coatings on hydrophobic films [26,27].

2. Experimental

Silica films were prepared via sol-gel technique. First, hydrophobic Me-SiO₂ sols were prepared using TEOS and MTMS as co-precursors. Two alkoxides (molar ratio TEOS/MTMS = 1) dissolved in C₂H₅OH were added in a bottle with H₂O and ammonia as catalyst in a single step, according to a previous report [28]. The solution was stirred continuously at 50 °C in a closed system for 8 h and then in an open system for 2 h to remove NH₃. The silicon wafers as substrates were heated at 550 °C in an oxidation furnace for one hour and formed SiO₂ layer on Si. The derived-sols (5 wt%) were then spin-coated at 5000 rpm for 30 s at room temperature on these silicon wafers, followed by firing at 400 °C under N₂ atmosphere for 30 min.

Three kinds of silica sols were prepared using hydrolysis-condensation of TEOS, BTESE and BTESO precursors. Ethanol was used as solvent and HCl was used as catalyst. The chemical structures of BTESE and BTESO consisted of a different number of -CH₂- chains, in the linking units between the two Si atoms, are shown in Fig. 2. The silica sols (2.5 wt%) were deposited on Me-SiO₂ films via spin-coating, followed by drying and firing at 300 °C under N₂ atmosphere for 30 min.

Asymmetric organosilica membranes were fabricated using porous α-alumina tubes (porosity: 50%, outside diameter: 10 mm) as supports. First, the Me-SiO₂ sols were deposited onto the macroporous supports, followed by firing at 400 °C under N₂ atmosphere. Then the layer was treated with H₂O/N₂ plasma (BPD-1H, SAMCO, Inc.) under a vacuum of 20 Pa pressure at room temperature using a power of 10 W. The flow rates of H₂O and N₂ were controlled at 15 and 10 ml/min, respectively. Finally, top layers were fabricated by coating BTESE and BTESO sols on Me-SiO₂ films, followed by drying and firing at 300 °C for 30 min. Gas permeance was measured as previously reported [13].

The morphology of the films was characterized by atomic force microscope (AFM, nanoscope, SII) in air with a non-contact mode,

and the scan size was 10 × 10 μm. The contact angle was measured with a Dropmaster (DM-300, Kyowa Interface Science Co., Ltd). The chemical structures were characterized at room temperature by Fourier transform infrared spectroscopy (FT-IR-4100, JASCO).

3. Results and discussion

All of the silica-derived sols from TEOS, BTESE, and BTESO formed homogenous and continuous films when spin coated on hydrophilic silicon wafers with a water contact angle (CA) of 30°. Fig. 3 shows that the CA of these films coated on silicon wafers was increased on the order of TEOS < BTESE < BTESO, the same trend as the increase length of the -CH₂- chains of these films (Fig. 2). TEOS and BTESE films showed a higher water affinity, which indicated a polar property and better compatibility with the ethanol solvent. BTESO with long chains of non-polar -CH₂- in the structure had a lower solubility in ethanol solvent. The topographic images of the three films are different, as shown in Fig. 4. The average roughness (AR) values of these films were analyzed by AFM. The BTESE film showed a highly smooth surface, with an AR of approximately 0.075 nm. The AR of TEOS film (2.8 nm) was similar to that of BTESE films and had the appearance of small sharp hills and valleys. The surface of BTESO film presented round protrusions with heights of several hundred nanometers and a large AR value of 79 nm. The length of the chains and compatibility of solvents and polymer played an important role in the surface morphology [15,19]. TEOS- and BTESE-derived sols had short chains and better solubility in ethanol, resulting in smooth and flat surfaces on silicon wafers. On the contrary, BTESO-derived sols had long chains and insufficient solubility in ethanol, and showed a high degree of roughness and protruding spheres.

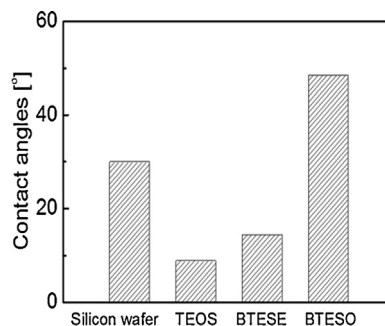


Fig. 3. Contact angles of TEOS, BTESE, and BTESO films spin-coated on silicon wafers and dried at room temperature.

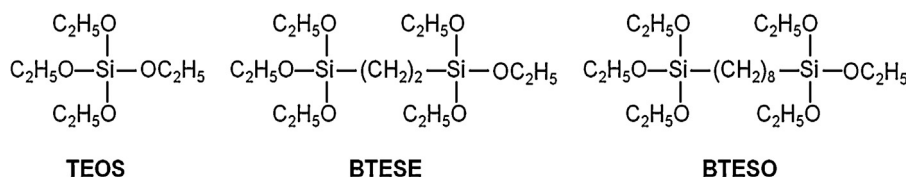


Fig. 2. Chemical structures of the silica precursors used in this work.

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