

Ambient Pressure Dried Silica Aerogel Thin Film from Water Glass

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ABSTRACT

A nano structured silica aerogel thin film was manufactured from inexpensive sodium silicate (water glass) using an ambient pressure drying method. High purity silicic sol was prepared by passing a water glass solution through an ion exchange resin, and the gel films were prepared on a modified glass substrate via dip coating. The dip coating conditions, such as coating time and solvent, were optimized. The optical and physical properties of the obtained silica aerogel thin film were characterized using a UV-visible spectrometer and a scanning electron microscope.

Key words: Water glass, Silica aerogel, Thin film, Ambient drying

1. Introduction

Silica aerogel is a highly porous material with pore diameters between 10 nm and 100 nm.¹⁾ With a porosity of 75~99% and nanometer pore size, aerogels are highly insulating materials with a thermal conductivity lower than that of air. However, due to several key limitations, only bulk silica aerogels have been used in practical applications. Also, it is very difficult to fabricate bulk aerogels as transparent as pure silica glasses using either a supercritical drying or an ambient pressure drying process. To date, silica aerogels have been manufactured using the supercritical drying method.²⁾ Supercritical aerogel processing is very energy intensive and often dangerous. Furthermore, metal alkoxides such as TMOS or TEOS, which are used as precursors, are toxic.³⁾ The present work introduces a new process, called ambient pressure drying, for the synthesis of aerogels.⁴⁾

A window coated with silica aerogel film, which is more transparent than a monolith aerogel, can be used in many applications in transparent super insulation materials. Two notable methods to fabricate insulating systems are (1) placing the aerogel between two layers of glass and (2) applying gas and granular silica aerogel in a double skin sheet.⁵⁾ The silica aerogel thin film has three times greater thermal conductivity than double-layered glass filled with argon. In this study, a silica aerogel thin film was prepared from an inexpensive water glass (sodium silicate) solution using an ambient pressure drying process. A wet gel film obtained by dip coating was prepared by solvent exchange and surface modification, similar to the aerogel monolith. The optical

and physical properties of the aerogel thin films were also investigated.

2. Experimental Procedure

The silica sols were prepared from a sodium silicate (water glass) solution. To make 8 wt% of silicate solution, 144 ml of water glass (Young Il Chemical, Korea; silica content 28~30 wt%, $\text{SiO}_2:\text{Na}_2\text{O}=3.52:1$) was mixed with 525 ml of distilled water. The diluted silicate solution was then passed through a column filled with an ion exchange resin (Amberlite, IR-120H, Rohm & Hass Co., USA) at a rate of 30 ml per minute. The prepared sol had a pH range of 2.4 to 2.8, and the silica content was estimated to be 5.4 wt%. A base catalyst (NH_4OH) was used to create silica sols with higher pH values of 3.5 or 4.0.

A glass substrate was placed in 10 vol% H_2SO_4 solution for 15 min, washed in acetone by ultra sonification for 15 min, and then washed in distilled water. Moisture was removed from the substrate surface using a N_2 gas gun. The surface-modified substrate showed improved wettability against the silica sol for coating. The gel coating was performed using a dip coating method. The coating speed at which the substrate was withdrawn from the silica sol was 7.7 cm/min. The coating was repeated one, three, and five times, which were dried in air for 30 sec. After dip coating, the coated substrate was held in a sealed container for 1 h at 50°C for gelation.

The gel films were aged in distilled water for 24 h at 50°C. Then, they were washed in acetone four times for 24 h at 50°C. The washed gel films were aged in a solvent (n-hexane (GR, >96%, Samchun Chemical, Korea), xylene (GR, 99.5%, Samchun Chemical, Korea), n-heptane (EP, 98%, Samchun Chemical, Korea), or toluene (GR, 99.5%, Samchun Chemical, Korea)) at 50°C. The solvents were replaced every 6 h

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during a period of 24 h. After aging, the gel films were chemically modified in 10 vol% TMCS/solvent solution for 24 h at 50°C and subsequently washed in the same solvents repeatedly for 1 day at 50°C in order to remove the remaining surface modification agents and reaction products, such as hydrochloric acid. The gel films were then dried in an oven at the boiling point of the solvent (n-hexane: 69°C, xylene: 142°C, n-heptane: 98°C, toluene: 110.6°C). The dried films were heat treated at 300°C for 3 h.

The surface morphology of the aerogel thin films was observed via a SEM (S-4200, Hitachi, Japan). The transmittance was measured via a UV-visible spectroscopy (V-570, Jasco, Japan) in a wavelength range between 200 nm and 900 nm.

3. Results and Discussion

The surface morphology of the aerogel thin films did not depend on the solvents used; however, their microstructure was dependent on the pH value of the precursor sol. When the pH value of the sol was lower than 3.5, the viscosity of the silica sol was extremely low, resulting in longer gelation times and a thinner gel coating layer. However, when the pH value of the sol was higher than 4.0, the gelation time was too short and the precursor sol gelled during the coating process. From these results, it can be inferred that the pH value is the most important parameter to be controlled when synthesizing a homogeneous aerogel thin film.

The surface microstructures of the aerogel thin film prepared using ambient pressure drying are shown in Fig. 1. The thin films of Figs. 1(a) and 1(b) were prepared from sols with pH values of 3.5 and 4.0, respectively. The size of the silica particles was approximately 20~30 nm, and the particles were linked three-dimensionally. The surface of the thin film obtained from the pH 3.5 sol was more porous than that fabricated with the pH 4.0 sol. Both the grain size and pore diameter of the silica aerogel thin films were slightly increased with the increasing pH value of the sol. In general, the sizes of the silica grains or pores of a wet gel depend on the polymerization conditions. If the pH is low or if salt is added, then the $\text{Si}(\text{OH})_4$ monomers tend to link with each other in chains. If the pH is higher than 7, then they remain separated and gradually grow.⁶⁾

Fig. 2 shows a cross-section micrograph of a thin film aerogel on the glass substrate. The thickness of the thin

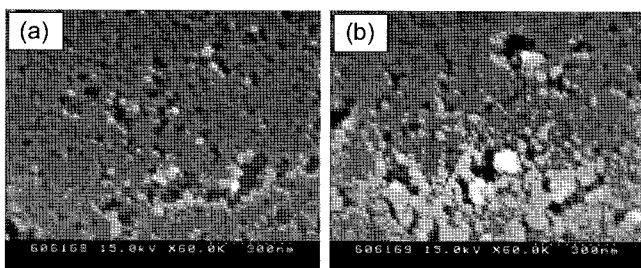


Fig. 1. Surface SEM photographs of aerogel thin films prepared from sols with (a) pH 3.5 and (b) pH 4.0. (solvent: n-Hexane).

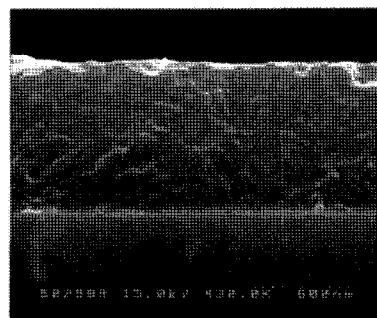


Fig. 2. Cross sectional SEM photographs of the thin film aerogel prepared from the sol with a pH of 3.5. (solvent: xylene).

film was approximately 1 μm . The thin film aerogel was continuous and uniform in thickness. As shown in Fig. 2, the thin film aerogel adhered strongly to the glass substrate and there was no sign that the aerogel would peel off from the substrates. In addition, macroscopic cracks were not observed in the surface of the thin film aerogel. Fig. 3 shows a SEM photograph of the microstructure of the thin film aerogel prepared with the pH 3.5 sol and subsequently heat treated at 300°C. There was no significant microstructural difference after the heat treatment at 300°C.

Fig. 4 shows a water drop picture on an aerogel thin film before and after the heat treatment. The as-dried thin film

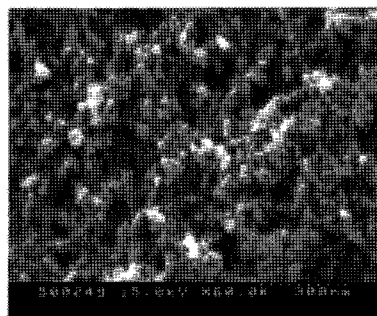


Fig. 3. Surface SEM photographs of the heat treated (300°C) thin film aerogel prepared from the sol with a pH of 3.5. (solvent: xylene).

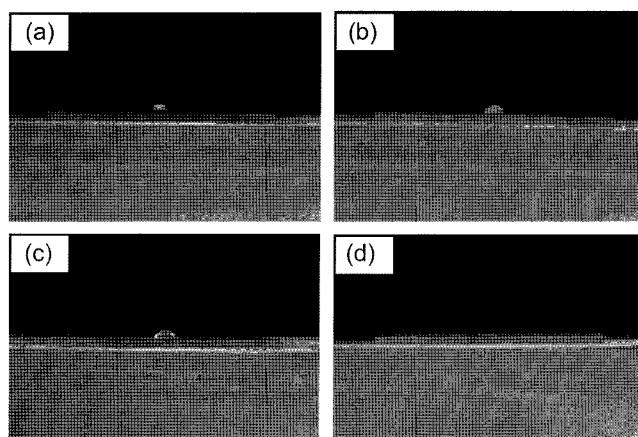


Fig. 4. Water drop on the thin film aerogels heat treated at (a) 80°C, (b) 200°C, (c) 300°C, and (d) 400°C.

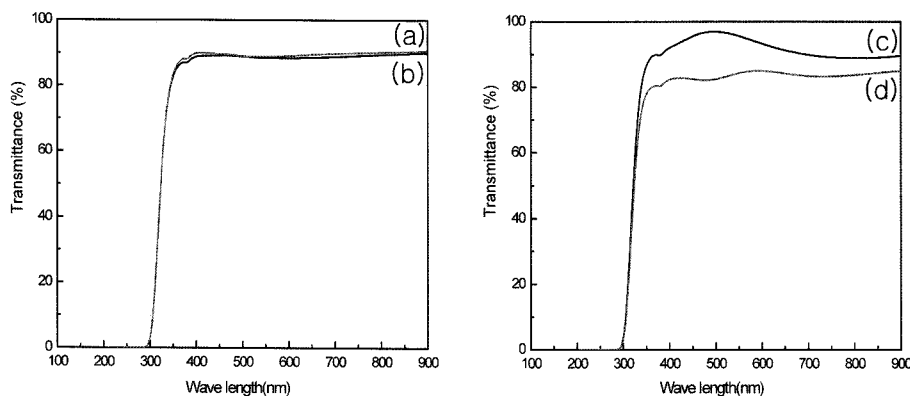


Fig. 5. Optical transmittance spectra of thin film aerogels prepared using various conditions: (a) pH=3.5, three coatings; (b) pH=3.5, five coatings; (c) pH=3.5, one coating; and (d) pH=4.0, one coating.

aerogel exhibited a high contact angle of approximately 120° . It was expected that TMCS would react with the pore water and Si-OH surface group of the silica wet gel to produce a hydrophobic Si-CH₃ terminal group on the silica surface. This phenomenon has been confirmed in our previous study.⁷ This indicates that the surface of the thin film is hydrophobic.

As the heat treatment temperature increased to 300°C , the contact angle was gradually decreased to 45° . It was found that the water completely wetted the surface of the aerogel heat treated at 400°C . This result suggests that the Si-CH₃ surface hydrophobic group evaporates slightly during the heat treatment and evaporates significantly around 400°C . The hydrophobic-to-hydrophilic transformation occurred between 300°C and 400°C . A previous study on an aerogel monolith has also reported that hydroxyl groups were replaced with hydrophobic methyl terminal groups in a silica network system near 400°C .⁸

Fig. 5 shows the optical transmittance spectra of the aerogel thin film and uncoated glass in the UV-visible range. The transmittance of the thin film was approximately 58% higher than that of the uncoated substrate. This finding might be associated with an anti-reflective effect exerted by the aerogel coating.⁹ While the surface morphology of the thin film was not related to the solvent type, the transmittance of the thin films was associated with the solvents and coating times. However, the transmittance of the thin film manufactured from the sol with a pH value of 3.5 is a few percent higher than that fabricated with a pH 4.0 sol.

4. Summary

Silica aerogel thin films were manufactured from an inexpensive water glass based silica sol via surface modification/solvent exchange and subsequent ambient pressure drying. From the surface microstructure investigation of the aerogel thin films, it was determined that the size of the silica particles and pore diameter in the silica network structure do not depend on the solvents, but depend significantly on the pH value of the silica sol. The transmittance of the aerogel thin film was as high as 90%, which is 5~8% higher

than that of the uncoated substrate, and varied depending on the pH value of the sol. The as-dried thin film was hydrophobic, and it was found that the surface chemical structure of the silica particles became hydrophilic when the film was heat treated above 300°C .

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