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Effects of vapor phase transport synthesis on the properties of porous silica films

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1. Introduction

Porous silica films, which are candidates for low dielectric constant (low-k) materials, suffer from their low mechanical strength. In order to have high mechanical strength, porous silica films with zeolite components have been studied [1-3]. Zeolites are microporous crystalline materials containing pores of a molecular scale so that the Young's modulus of zeolites (100 GPa) has larger than that of dense silica (70 GPa) though the density of zeolites (e.g., 1.76 g/cm^3 for silicalite) has lower than that of dense silica (2.2 g/cm^3). In our previous work, ZSM-48 zeolite was synthesized by the vapor phase transport (VPT) method [4], which is one of the dry gel conversion methods [5]. In this work, the effects of VPT synthesis on the properties of the porous silica films are investigated.

2. Experimental

Fig. 1 shows the preparation procedure, which consists of a sol-gel technique based on the self-assembling of surfactant templates [6] and the VPT synthesis. A precursor solution was prepared by the mixture of silica precursor tetraethoxysilane (TEOS), catalyst nitric acid, water, solvent ethanol and surfactant template. The solution was deposited on a Si (100) wafer by a spin-coating method to form a homogeneous thin layer and cured at 150˚C for 1 min under nitrogen ambient. Fig. 2 shows the schematic diagram of an autoclave for the VPT synthesis. The autoclave had a perforated plate in the middle of the vessel. A liquid phase mixture of ethylenediamine (EDA), triethylamine (Et_3N) and water filled the bottom of the autoclave. The surfactant template and silica precursor deposited on the wafer were set on the plate. The autoclave was heated up to 200˚C and kept at that temperature during synthesis. They were exposed to the vapor mixture under an autogenous pressure. As-synthesized products were rinsed with acetone and blow-dried with nitrogen and were calcined at 400˚C for 4 hours in dry air. A heating rate of 1˚C/min was adopted.

In order to measure the electric properties, a MIS capacitor structure was fabricated by direct current magnetron sputtering. The leakage current voltage and capacitance voltage measurements are carried out after 300˚C baking for 2 hours at nitrogen ambient environment with humidity 1.0% RH in order to remove water in the films.

3. Results and Discussion

Fig. 3 shows SEM pictures (top view) of the samples synthesized by VPT method for 8 days with water content of 0wt% (a), 5wt% (b) and 30wt% (c). No objects were formed on the surface of the films with 0wt% water content as shown in Fig. 3(a). Thin needle crystals (15 μm in length, 0.5 μm in diameter) were formed on the surface of the film with 5wt% water content as shown in Fig. 3(b). Stick-like crystals (45 μm in length, 1.5 μm in diameter) were formed on the surface of the film with 30wt% water content as shown in Fig. 3(c).

Fig. 4 shows XRD patterns of the samples synthesized by VPT method for 8 days with water content of 0wt%, 5wt% and 30wt%. The diffraction pattern of the sample with 30wt% water content was assigned to that of ZSM-48 zeolite [7]. Fig. 5 shows the framework view of ZSM-48 zeolite, which has a one-dimensional 10-membered ring channels with a diameter of 5.6 Å× 5.3 Å.

FTIR absorption spectra of the samples synthesized by VPT method for 8 days with water content of 0wt%, 5wt% and 30wt% are shown in the range of 400-700cm^{-1} (Fig. 6), 1000-1350cm^{-1} (Fig. 7) and 2800-4000cm^{-1} (Fig. 8), respectively. In Fig. 6, the absorption peak at ~550cm^{-1} of the sample with 30wt% water content was assigned to the presence of the 5-membered ring in the framework and characteristics for the structure of ZSM-48 zeolite. The other peak at ~470cm^{-1} was attributed to the Si-O bend and was not structure sensitive. The absorption peaks at ~1070cm^{-1}, which are assigned to Si-O-Si asymmetric stretching mode, was shifted to higher wavenumber by the VPT process as shown in Fig. 7. The broad absorption band related to O-H stretching bonds in the range of 3000-3800cm^{-1} and the absorption peak at 3740cm^{-1} related to the isolated Si-OH bond were suppressed by the VPT process as shown in Fig.8.

Figs. 9 and 10 show the percentage of film shrinkage and refractive index for the samples with water content of 0wt%, 5wt% and 30wt% as a function of VPT time, respectively. Compared with the sample without VPT process, the film shrinkage and refractive index could be suppressed by the VPT process.

Figs. 11 and 12 show the leakage current and the dielectric constant for the samples with water content of 0wt%, 5wt% and 30wt% as a function of VPT time, respectively. The VPT process with 0wt% water content suppressed the leakage current by an order of 10^{-10} (A/cm^2) and reduced the dielectric constant to 70%.

4. Summary

The effects of vapor phase transport synthesis on the properties of the porous silica films were investigated. The VPT process changed the skeletal structure of silica and made the sample hydrophobic. The VPT process with 0wt% water content suppressed the leakage current and reduced the dielectric constant. Consequently, the VPT method can be applied to the low-k dielectric film formation process for hydrophobicity.

References

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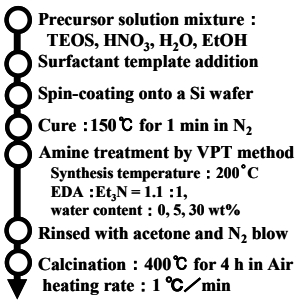

Fig. 1. Preparation procedure

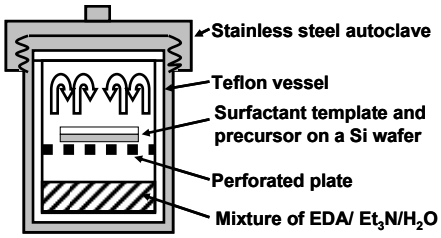

Fig. 2. Schematic diagram of an autoclave for VPT synthesis

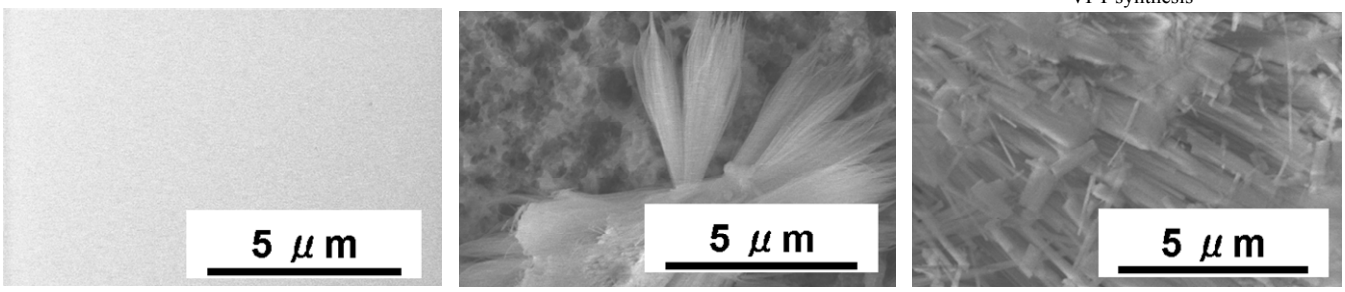

Fig. 3. SEM pictures (top view) of the samples synthesized by VPT method for 8 days with water content. (a) 0 wt%. (b) 5 wt%. (c) 30 wt%.

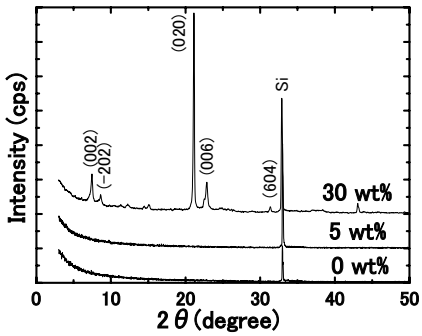

Fig. 4. XRD pattern of the samples synthesized for 8 days with water content of 0, 5 and 30wt%

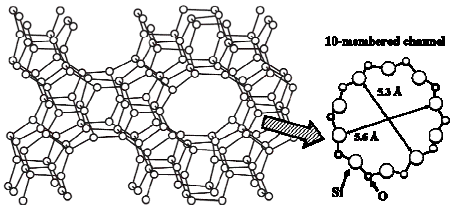

Fig. 5. Framework structure of ZSM-48 zeolite

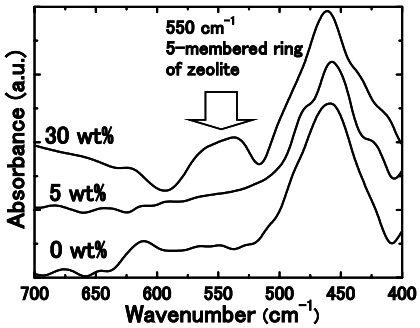

Fig. 6. FTIR spectra of the samples synthesized for 8 days with water content of 0, 5 and 30wt%

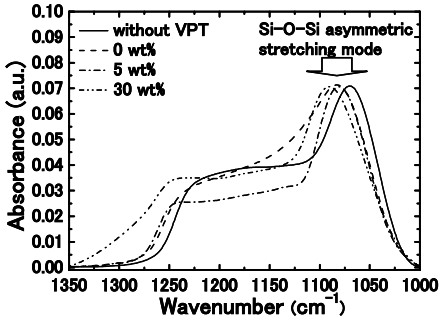

Fig. 7. FTIR spectra, in the range of 1350-1000cm^{-1}, of the samples synthesized for 8days.

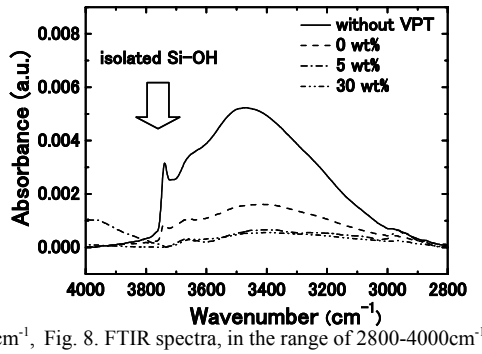

Fig. 8. FTIR spectra, in the range of 2800-4000cm^{-1}, of the samples synthesized for 8days.

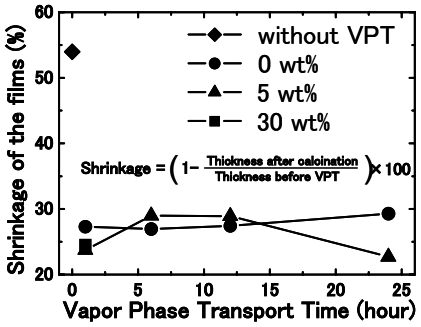

Fig. 9 Film shrinkage as a function of vapor phase transport time

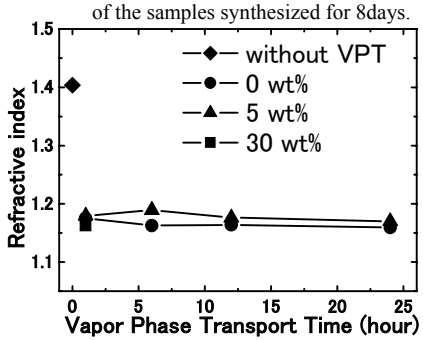

Fig.10. Refractive index as a function of vapor phase transport time

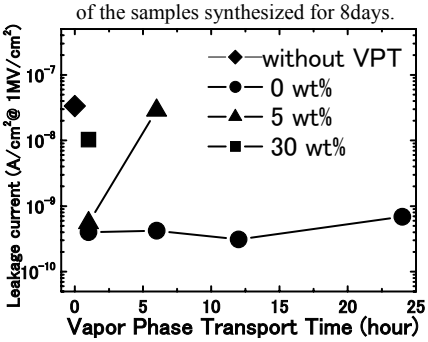

Fig. 11. Leakage current as a function of vapor phase transport time

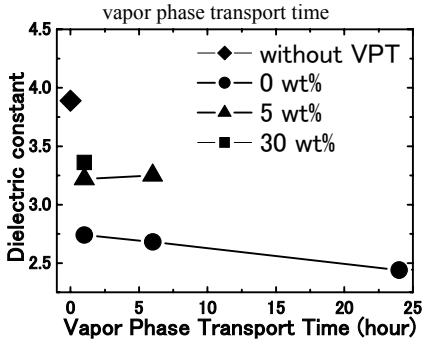

Fig. 12. Dielectric constant as a function of vapor phase transport time