

Silylation Hardening for Mesoporous Silica Zeolite Film

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ABSTRACT

Pure silica zeolite films were formed for ultra-low-k interlayer dielectrics in ultra-large integrated circuits. Hydrothermal crystallization and vapor phase transport synthesis methods were developed. Self-assembled mesoporous silica was formed by use of a surfactant. Silylation hardening was achieved by 1,3, 5, 7 tetramethylcyclotetrasiloxane (TMCTS) vapor treatment. The zeolite formation by hydrothermal crystallization and vapor phase transport can reduce O-H bond in the silica films, resulting in the reduction of leakage current by a factor of 1/10. The TMCTS vapor treatment can reduce the leakage current by 4 orders of magnitude due to the decrease of Si-OH and O-H bonds. The elastic modulus of 5.18 GPa and the dielectric constant of 1.96 were achieved simultaneously by TMCTS silylation hardening process for the mesoporous silica zeolite thin film.

Keywords: silylation, zeolite, surfactant, low-k, mesoporous silica

1 INTRODUCTION

In order to overcome problems of signal delays in interconnects in ultra-large scale integrated circuits (ULSI), low-dielectric-constant (low-k) interlayer dielectric films are needed. Mesoporous silica whose pore sizes are ranging from 2 nm to 10 nm has been studied as a potential candidate for ultra low-k materials¹. However, mechanical strength of the low-k film is degraded when mesosized pores are introduced into skeletal materials to reduce the film density. Zeolite is a promising candidate as an advanced low-k material²⁻⁴, which has microporous crystalline structure so that the Young's modulus (100 GPa) is larger than that of dense silica (70 GPa) and the density (e.g., 1.76 g/cm³ for silicalite) is lower than that of dense silica (2.1-2.3 g/cm³).

In this paper, pure-silica zeolite films are prepared by hydrothermal synthesis and vapor phase transport (VPT) methods, and the effect of silylation on electrical and mechanical properties are investigated.

2 ZEOLITE FORMATION

2.1 Hydrothermal Crystallization

The precursor solution of tetra-butyl ammonium hydroxide (TBAOH), tetraethyl orthosilicate (TEOS) and

ethyl alcohol (EtOH) were mixed and stirred at the room temperature. Hydrolysis of TEOS was caused by EtOH. The precursor was heated in an autoclave for 110 hours at 100°C, then cooled down to the room temperature, and heated up again for 10 hours at 100°C. The suspension prepared by the hydrothermal crystallization method contained zeolite nanoparticles.

To reduce the k-value, butanol and a surfactant of ethylene oxide propylene oxide ethylene oxide triblock copolymer, (EO)₁₃(PO)₂₀(EO)₁₃, were added to the suspension while stirring so that mesoscopic size pores of several nm in diameter were formed. The zeolite silica film was formed on a Si wafer by spin coating. After the film was pre-baked on a hot plate for one hour at 90°C, it was calcined at 400°C in air and annealed at 400°C for 5 h. TMCTS vapor treatment was carried out at 400°C and annealed in the N₂ atmosphere so that the inner pore wall surface was silylated by TMCTS molecules, forming polymer cross-linking network.

2.2 Vaporphase Transport

A precursor solution was prepared by use of TEOS, catalyst nitric acid, water and EtOH. Surfactant template Brij78[®] (Polyethylene glycol stearyl ether C₁₈H₃₇(OCH₂CH₂)₂₀OH) and the precursor solution were mixed. The final molar ratio of the solution was TEOS: Brij78: H₂O: HNO₃ = 1:0.01:10:0.01. The resulting 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.

The VPT was carried out in an autoclave in which a wafer with spin-coated silica film was set on a perforated plate in the middle of the vessel. A liquid phase mixture of ethylenediamine (EDA), triethylamine (Et₃N) and water, filled the bottom of the autoclave. The autoclave was heated up to 200°C and kept at that temperature during synthesis. They were exposed to the vapor mixture of EDA, Et₃N and water under an autogenous steam 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.

3 RESULTS AND DISCUSSION

Figure 1 shows the framework view of ZSM-48 zeolite, which has a one-dimensional 10-membered channel with a

diameter of $5.6 \text{ \AA} \times 5.3 \text{ \AA}$. Figure 2(a) shows the results of the XRD patterns. The diffraction peaks of Sample No. 1 and 2 matched those of ZSM-48 zeolite, which has two groups of the polytypes: monoclinic unit cell and orthorhombic unit cell. The measured XRD patterns showed only two peaks at 7.54° and 8.74° at low angle so that the zeolite crystal was the orthorhombic unit cell having parameters of $a = 24.66 \text{ \AA}$, $b = 8.4 \text{ \AA}$, $c = 24.66 \text{ \AA}$ and $\beta = 109.47^\circ$. Figure 2(b) shows the XRD patterns of the samples synthesized by the VPT method (Sample No. 1, 5, 6 and 7).

Figure 3(a) shows the FTIR spectra of the samples synthesized by the VPT method (Sample No. 1, 4, 5, 6, 7 and 8). The spectrum of sample No. 8 is formed by the sol-gel technique and spin-coating method. For sample No. 2, 6 and 7, the absorption peak was not observed around 550 cm^{-1} , which is assigned to the presence of the 5-membered ring of tetrahedral SiO_2 in the framework and characteristic structure of ZSM-48 zeolite. Another peak around 470 cm^{-1} was attributed to the Si-O symmetric bend and was not structure sensitive. In Fig. 3(b), the broad absorption band related to O-H stretching bonds between 3000 cm^{-1} and 3800 cm^{-1} , and the absorption peak at 3740 cm^{-1} related to the isolated Si-OH bond were observed. The absorption peaks of O-H bonds were suppressed effectively for samples 2, 6 and 7, so that ZSM-48 zeolite was intrinsically hydrophobic.

Figure 4 shows the film thickness and refractive index as a function of the VPT time for the sample 4, 5 and 8. The VPT time equal zero denotes the sample formed by the sol-gel technique and spin-coating method. This result showed that the film shrinkage was suppressed by the VPT method.

Figure 5 shows the dielectric constant at 1 MHz and the leakage current density at 1 MV/cm as a function of the VPT time for the sample 4, 5 and 8, which were obtained from IV and CV measurements. The dielectric constant decreased to 2.7 with increasing vapor phase transport time and the leakage current was suppressed to an order of $10^{-8} \text{ (A/cm}^2\text{)}$. Reductions of the dielectric constant and the leakage current were caused by the hydrophobicity obtained from the contribution of EDA, Et_3N and water.

MEL type zeolite which has 10 membered ring whose pore diameters are 0.53 and 0.54 nm was made by a hydrothermal crystallization method as shown in Fig. 6. The existence of zeolite was confirmed by the absorption peak around 560 cm^{-1} which is associated with an asymmetric stretching mode of five-membered ring blocks in MEL-type zeolite skeletal¹³ as shown in Fig. 7.

The pore wall surface was silylated by TMCTS molecules that reacted with Si-OH groups on the pore wall surface as shown in Fig. 8 (a), and formed the polymer cross-linking network as shown in Fig. 8 (b).

FT-IR absorbance spectra of zeolite and porous silica with and without silylation were compared as shown in Fig. 9. A broad absorption in zeolite around 3513 cm^{-1} , which is associated with the O-H group, was less than that of porous silica film. Both absorptions by isolated Si-OH at 3745 cm^{-1}

and the O-H group were dramatically decreased by the silylation treatment. Furthermore, the existence of C-H, SiHCH_3O_2 and SiHO_3 bonds were exhibited in Fig. 9, indicating the film hydrophobic. Pore size distribution was calculated from the measurement of SAXS as shown in Fig. 10. The pore distribution of about 4 nm due to the surfactant was confirmed, but zeolite micropores of 0.5 nm could not be identified by SAXS. The distribution of meso-sized pores slightly decreased from 4.512 nm to 4.399 nm by the TMCTS treatment because the pore surface was covered with cross-linked TMCTS molecules.

The dependences of porosity on the surfactant concentration of the zeolite film and porous silica film were shown in Fig. 11(a). Figure 11(b) shows the dielectric constant versus surfactant concentration. Zeolite shows lower dielectric constants than porous silica and its dielectric constant decreased from 2.206 to 1.962 by silylation.

Elastic modulus of zeolite increased from 3.312 to 5.180 GPa by the TMCTS treatment as shown in Fig. 12. The dielectric constant of 1.96 was achieved with the elastic modulus of 5.18 GPa for TMCTS silylated porous zeolite film. Figure 13 shows Weibull plot for the life time of time dependent dielectric breakdown (TDDB). The life time of zeolite with silylation was longer than the porous silica with silylation by a factor of approximately 2.5.

4 CONCLUSION

Zeolite formation by hydrothermal crystallization and the VPT can reduce O-H bond in the silica films, resulting in the reduction of leakage current by a factor of 1/10. The TMCTS vapor treatment can reduce the leakage current by 4 orders of magnitude due to the decrease of Si-OH and O-H bonds. The elastic modulus of 5.18 GPa and the dielectric constant of 1.96 were achieved simultaneously by TMCTS silylation hardening process.

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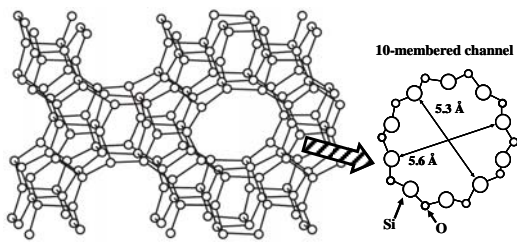


Fig. 1. A schematic diagram of ZSM-48 zeolite framework.

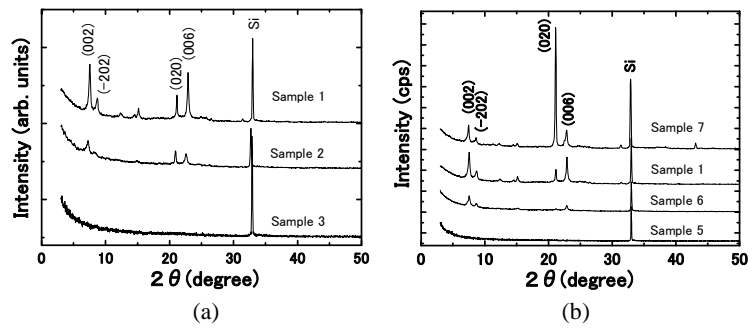


Fig. 2. XRD patterns for ZSM-48 zeolite films formed by vapor phase transport method. (a) Sample No. 1, 2, and 3. The mixture ratio of EDA: Et3N: H2O are 1: 2: 1, 2: 1: 1 and 1: 1: 2, respectively. (b) Sample No. 1, 5, 6, and 7. The mixture ratio of EDA: Et3N: H2O is 1: 2: 1. Synthesis times are 6days, 2hours, 4days, and 8 days, respectively.

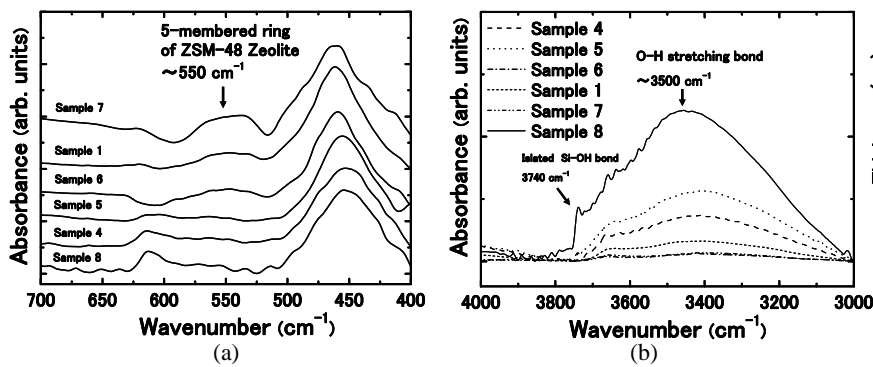


Fig. 3. FTIR spectra of the samples synthesized by the VPT method (Sample No. 1, 4, 5, 6, 7 and 8). (a) The absorption peak around 550 cm⁻¹ related to the 5-membered ring of ZSM-48 zeolite. (b) The absorption peak related to O-H stretching bonds and isolated Si-OH bond.

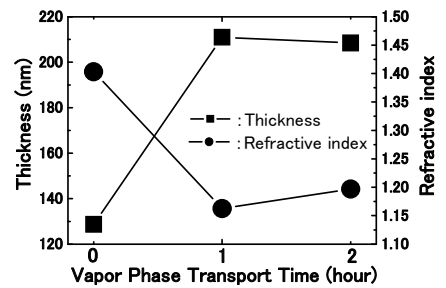


Fig. 4. Film thickness and refractive index of the sample synthesized by the VPT method as a function of vapor phase transport time for the sample 4, 5 and 8. Sample No. 8 was formed by the sol-gel technique and spin-coating method without VPT.

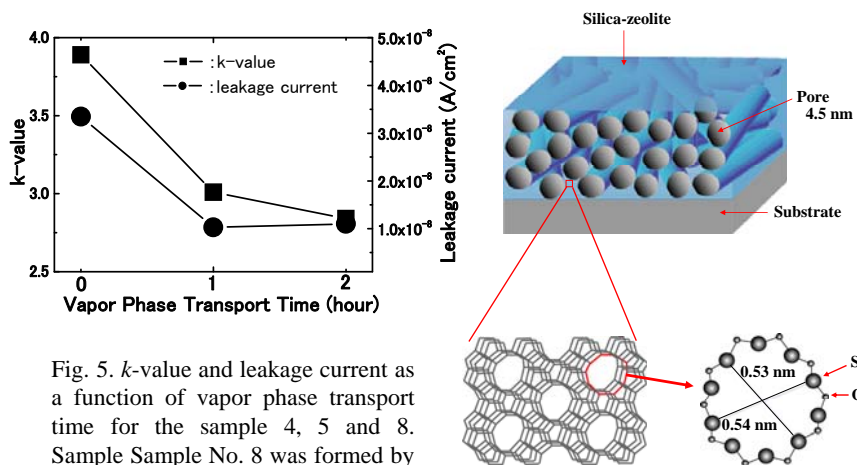


Fig. 5. *k*-value and leakage current as a function of vapor phase transport time for the sample 4, 5 and 8. Sample No. 8 was formed by the sol-gel technique and spin-coating method without VPT.

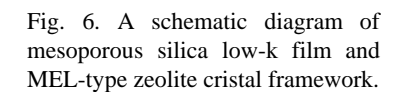


Fig. 6. A schematic diagram of mesoporous silica low-k film and MEL-type zeolite crystal framework.

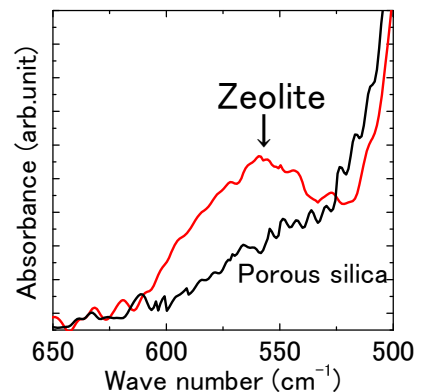


Fig. 7. Fourier transform FT-IR spectra of MEL type pure silica zeolite which was formed by hydrothermal crystallization method.

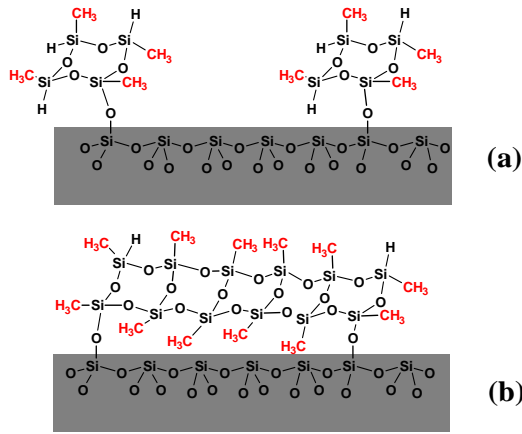


Fig. 8. Schematic illustration of silylation for inner surfaces of porous silica. (a) Adsorption of tetramethylcyclotetrasiloxane (TMCTS). (b) After cross linking of TMCTS.

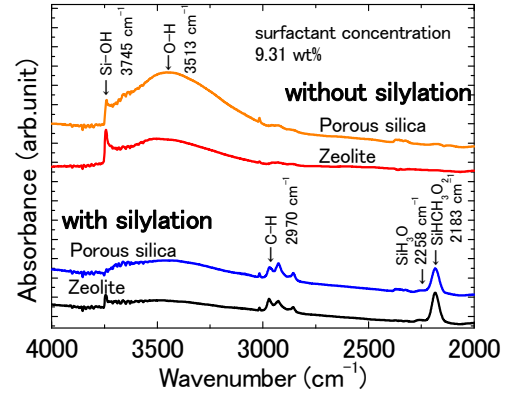


Fig. 9. FT-IR spectra of zeolite and porous silica films with and without TMCTS silylation.

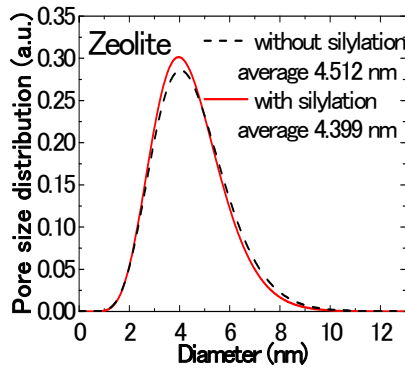


Fig. 10. Pore size distribution of zeolite films with and without TMCTS silylation.

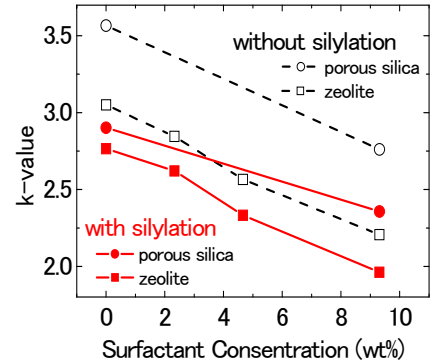
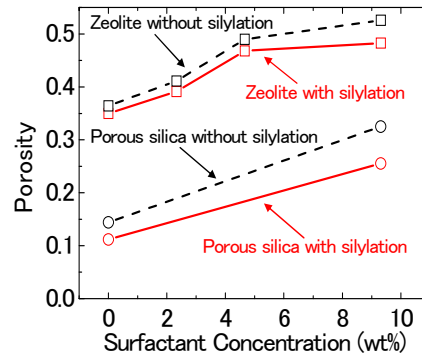


Fig. 11. Dependence of surfactant concentration for zeolite and porous silica films with and without TMCTS silylation. (a) Porosity versus surfactant concentration. (b) k-values versus surfactant concentration.

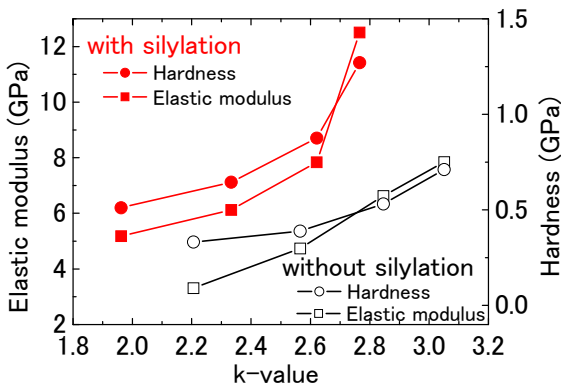


Fig. 12. Elastic modulus and hardness versus dielectric constant for zeolite and porous silica films with and without TMCTS silylation.

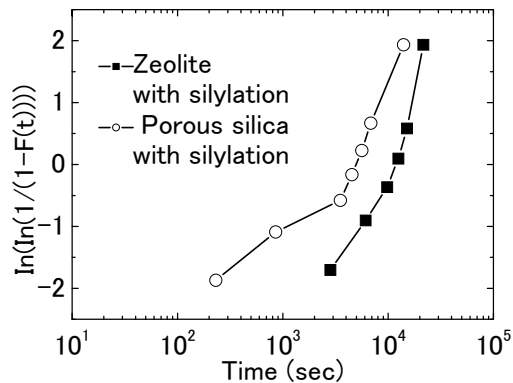


Fig. 13. Weibull plot of time dependent dielectric breakdown life time at 3.6 MV/cm in 200°C for zeolite and porous silica films with TMCTS silylation.