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## Effects of Silylation on Electrical and Mechanical Characteristics of Mesoporous Pure Silica Zeolite Films

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### 1. Introduction

Pure silica zeolite film is a promising candidate as an advanced low-dielectric-constant (low-k) interlayer dielectric because its mechanical strength is higher and the film density is lower than those of quartz due to its crystalline silica skeletal with micropores [1-3]. In this paper, we studied the effects of silylation on film properties of pure silica zeolite dielectrics.

### 2. Experimental

The MEL type zeolite was formed by the process flow as shown in Fig. 1. The precursor solution of tetra-butyl ammonium hydroxide (TBAOH), tetraethyl orthosilicate (TEOS), and ethyl alcohol were stirred for 24 h. The mixture was heated in autoclave for 110 h at 100°C (hydrothermal synthesis). The precursor was then cooled down to room temperature, and heated again for 10 h at 100°C. Two-stage synthesis improves the yield for zeolite nanocrystal without changing the particle size [4]. For comparison, the precursor solution without the hydrothermal synthesis was prepared for porous silica formation. After butanol and the surfactant (EO)<sub>13</sub>(PO)<sub>20</sub>(EO)<sub>13</sub> were added to the suspension, the film was formed by spin coating on a Si wafer, and calcined in air for 5 h at 400°C. The film was then annealed in the tetramethylcyclotetrasiloxane (TMCTS) atmosphere at 400°C [5]. By this treatment, the pore wall surface was silylated by TMCTS molecules that reacted with Si-OH groups, and formed the polymer cross-linking network as shown in Fig. 2 [5].

### 3. Results and Discussion

Figure 3 compares the Fourier-transform infrared (FTIR) absorbance spectra of pure silica zeolite and porous silica films. The existence of MEL-type zeolite was confirmed by the absorption around 560 cm<sup>-1</sup> [2, 3, 6].

Figures 4 shows the dependence of refractive index and porosity on the surfactant concentration. The porosity  $x$  was calculated by using Lorentz-Lorenz expression:

$$x = 1 - \frac{(n^2 - 1)(n^2 - 1)/(n^2 + 2)}{(n_{SiO_2}^2 - 1)/(n_{SiO_2}^2 + 2)}, \quad (1)$$

where  $n$  and  $n_{SiO_2}$  are refractive indexes of dielectric film and SiO<sub>2</sub>, respectively. The porosity increased with increasing the surfactant concentration, while it decreased by 10% with TMCTS treatment. Furthermore, the porosity of zeolite is 4-fold that of porous silica without hydrothermal synthesis. The decrement of porosity by the TMCTS treatment was understood from the pore size distribution obtained from the small angle X-ray scattering (SAXS) spectroscopy. That is, the average pore size slightly decreased from 4.512 nm to 4.399 nm by the TMCTS treatment as illustrated in Fig. 5. This is because pore surface was covered with cross-linked TMCTS molecules.

In Fig. 6, we compared the FT-IR absorbance spectra of zeolite and porous silica with and without silylation. A broad absorption in zeolite around 3513 cm<sup>-1</sup>, which is associated with the O-H group, is weaker than that of the porous silica film. Both of the absorption by isolated Si-OH at 3745 cm<sup>-1</sup> and the broad O-H group were dramatically decreased by the silylation treatment. Furthermore, the existence of C-H, SiHCH<sub>3</sub>O<sub>2</sub> and SiHO<sub>3</sub> bonds were exhibited (Fig. 6 (b)), indicating the films became hydrophobic. The dielectric constant was decreased from 2.206 to 1.962 by the silylation as plotted in Fig. 7, and the leakage current was decreased by 4 orders of magnitude at 2 MV/cm as shown in Fig. 8. The variation of k-value is consistent with the increment of the porosity and reduction of OH-related absorption after the TMCTS treatment. The leakage current is also attributed by the reduction of OH-related absorption, resulting in dramatic decrease of an ionic current component [7].

As clearly observed, dielectric constant and leakage current of pure silica zeolite film was lower than those of porous silica film under the present process conditions. It is suggested that the hydrothermal synthesis is necessary to construct the Si-O network sufficiently.

Elastic modulus measured by nano-indenter for pure silica zeolite film increased from 3.312 to 5.180 GPa by the TMCTS treatment as shown in Fig. 9. The silylation treatment possibly passivates mechanically weak defects on pore wall surfaces by forming polymerized network as shown in Fig. 2 and Fig. 6 [5].

### 4. Conclusion

A pure silica zeolite film was successfully obtained with a hydrothermal synthesis. The zeolite film showed lower dielectric constant and lower leakage current than porous silica films that obtained without hydrothermal synthesis. In zeolite, both of the dielectric constant and the leakage current also decreased by the silylation with TMCTS. The TMCTS treatment is effective not only for reducing leakage current but also for increasing mechanical strength of porous zeolite by forming the polymerized network which eliminates water adsorption and passivates defects on the pore wall surfaces.

### References

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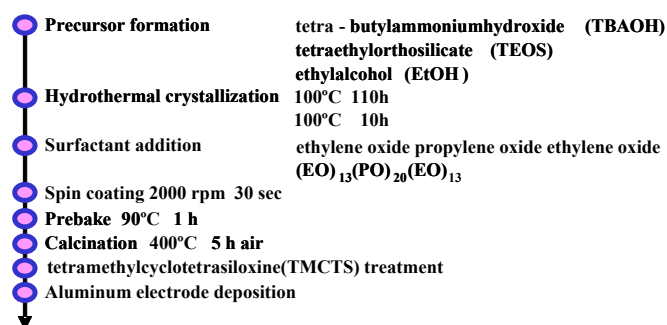


Fig.1. Process flow of pure silica zeolite film formation.

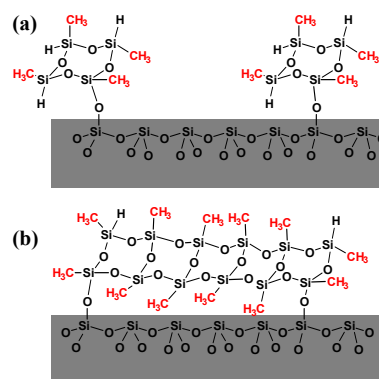


Fig.2. Schematic illustration of adsorption of TMCTS (a) and its cross-linking (b) [3].

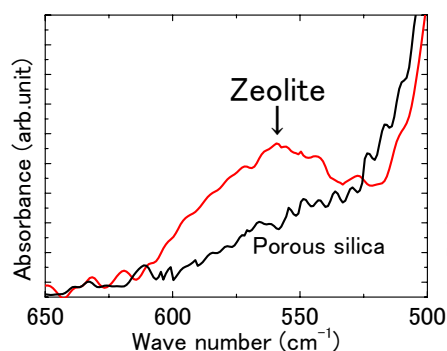


Fig. 3. Fourier transform infrared spectra of pure silica zeolite and porous silica films.

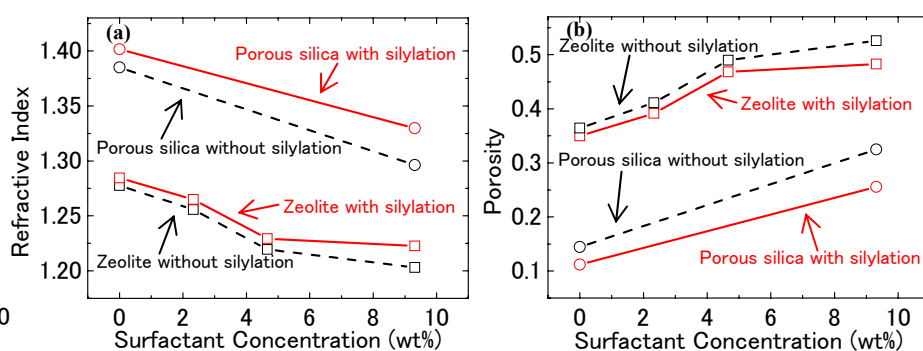


Fig. 4. Dependence of surfactant concentration of (a) refractive index versus surfactant concentration and (b) porosity versus surfactant concentration.

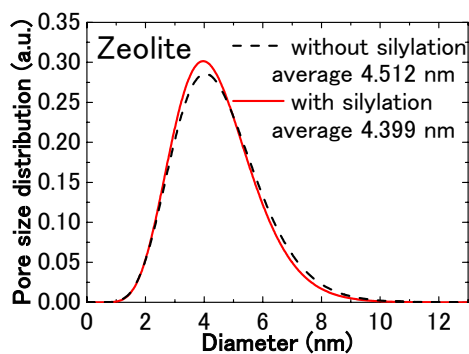


Fig. 5. Pore size distribution of zeolite films with and without silylation.

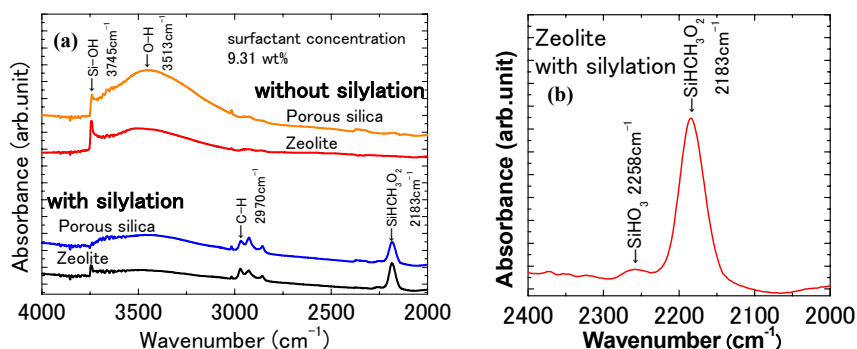


Fig. 6. Fourier transform infrared spectra of zeolite and porous silica films with and without silylation (a) and in an expansion scale around 2200 cm<sup>-1</sup> (b).

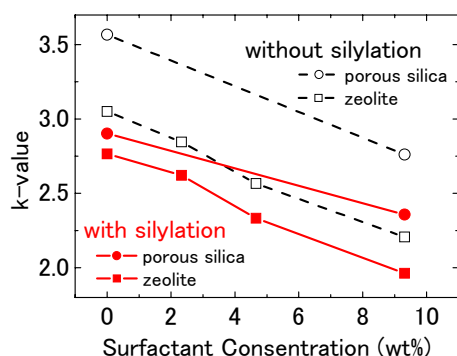


Fig. 7. Dielectric constants versus surfactant concentration for pure silica zeolite and porous silica films.

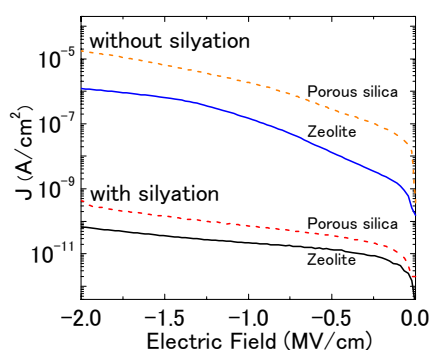


Fig. 8. Leakage current versus electric field for pure silica zeolite and porous silica films with and without silylation.

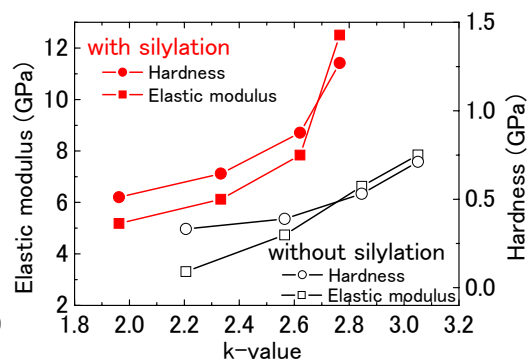


Fig. 9. Elastic modulus and hardness versus dielectric constant for pure silica zeolite and porous silica films with and without silylation.