

Low-*k* Mesoporous Pure Silica Zeolite Synthesis with Centrifugation Process of Zeolite Precursor

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1. Introduction

Low dielectric constant (Low-*k*) materials have been required for higher signal processing of ultra large scale integrated circuits (ULSIs). Pores have been introduced to the low-*k* materials for lowering its dielectric constant, and however pores also have weakened its mechanical strength. The design of skeleton and pores of the low-*k* is critical issue for fabricating ULSIs. Pure silica zeolite with pores of sub-1 nm has been suggested for low-*k* [1]. The pure silica zeolite has zeolite microcrystals inside the film, and this microcrystal strengthens its hardness [2-3].

In this paper, centrifugation process of zeolite precursor was discussed. By use of centrifugation, the dielectric constant of pure silica zeolite film became smaller, and breakdown electric field became larger. And low-*k* pure silica zeolite film with *k*= 2.0 and breakdown electric field of 3.3 MV/cm was successfully obtained.

2. Experimental

Synthesis and fabrication process of low-*k* mesoporous pure silica zeolite film was shown in Fig. 1. Precursor was synthesized with Tetrabutylammoniumhydroxide (TBAOH), tetraethoxy -silane (TEOS), ethylalcohol (EtOH) and deionized (DI) water. After aging in room temperature, the solution was subject to two-step hydrothermal syntheses, at first the precursor was synthesized in a low temperature for nucleation of zeolite crystal, and in the second the precursor was synthesized in a high temperature for crystal growth: the precursor was heated in an autoclave for 48 h at 60°C, and was cooled down to the room temperature, and heated up again for 120 h at 85°C. Two-step synthesis improves the yield for zeolite nanocrystal without changing the particle size [4]. The handling of precursor and centrifugation was shown in Fig. 2. After the centrifugation process for 3000, 6000, 9000 rpm, 1-butylalcohol (1-BtOH) and surfactant (Brij 78) were added to the suspension with stirring, so that mesoscopic size pores of several nm, in diameter were formed, which reduce the *k*-value of the zeolite film. The synthesized zeolite precursor was spin-coated on Si wafer at room temperature. The films were prebaked at 90°C in air. Next, the films were cured at 400°C for 5 h in N₂. Schematic of the film surface was shown in Fig. 3. To evaluate the electrical properties of the low-*k* film, Aluminum electrodes were formed on the top of the samples using vacuum vapor deposition.

3. Results and Discussion

Diameter distribution of zeolite crystal after hydrothermal synthesis was measured with dynamic light scattering (DLS) for inspection of another zeolite crystal. The result is shown in Fig. 4. Two peaks at around 10 nm and 200 nm appeared

typically. The 10 nm peaks corresponds silica cluster, and the 200 nm corresponds zeolite crystal. The reproduced the peaks of the zeolite which was synthesized in 85°C [5]. Figure 5 (a) shows Fourier-transform infrared (FT-IR) absorbance spectra of pure silica zeolite and porous silica films. The zeolite peak was observed at 560 cm⁻¹. Fig. 5 (b), (c) shows FT-IR absorbance spectra of siloxane bond. It is found that amount of binding was changed by centrifugation conditions. Highest peak was found at 3000 rpm. When centrifugation conditions are too high, the peak of the siloxane is lower than the reference. Figure 6 shows the dielectric constant as a function of the centrifugation. By use of centrifugation process, the dielectric constant decreased, and at 3000 and 6000 rpm, *k*= 1.92 and 2.0 were achieved respectively. Figure 7 shows leakage current characteristics of each centrifugation. Low leakage current of 10⁻⁹ A/cm² at 1 MV/cm was achieved. Figure 8 shows Weibull plot of breakdown field strength. At the reference sample, the breakdown electric field was 2.36 MV/cm. By applying of centrifugation process, the breakdown electric field became larger, and at 3000 rpm of centrifugation process, 3.3 MV/cm was achieved. The zeolite low-*k* film formation was relatively stable when 3000 rpm centrifugation was applied. On the contrary at 9000 rpm, degradation of the breakdown electric field was occurred.

4. Conclusion

A low-*k* pure silica zeolite film was successfully obtained with a hydrothermal synthesis and centrifugation process. Reduction of dielectric constant and improvement in field strength was achieved by centrifugation of the zeolite precursor. By use of 3000 rpm centrifugation process, low-*k* pure silica zeolite film with *k*= 2.0 and breakdown electric field of 3.3 MV/cm was successfully obtained. This mesoporous pure silica zeolite low-*k* film is useful for high performance beyond 22 nm-node ULSIs.

References

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- **Precursor formation**
TBAOH: 19.8 ml, TEOS: 20 ml, EtOH : 23.5 ml, DIW : 14 ml
- **Hydrothermal crystallization**
(1) 60°C 48 h, (2) 85°C 120 h
- **Centrifugation**
3000, 6000, 9000 rpm 30 min
- **Surfactant addition**
Precursor : 1-BtOH : (Brij 78 : 6 g + EtOH 30 ml) = 3 : 3 : 2
- **Spin coating**
2000 rpm 30 s
- **Prebake**
90°C 1 h
- **Calcination**
N₂ ambient, 400°C, 5 h

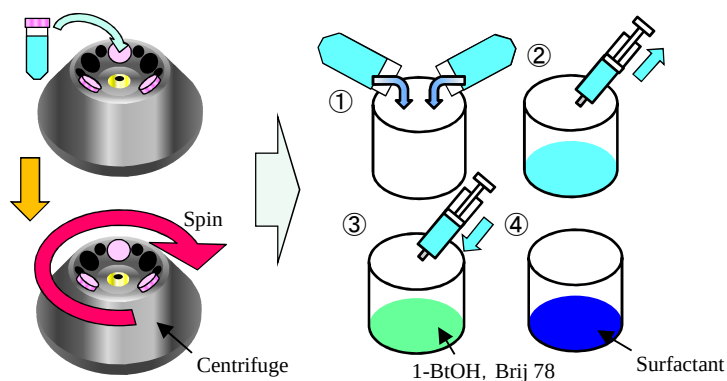


Fig. 2. The handling of precursor and centrifugation

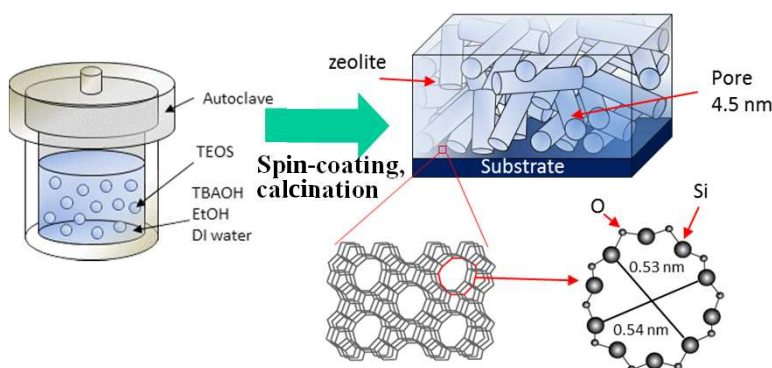


Fig. 3. Hydrothermal synthesis method and pure silica zeolite film

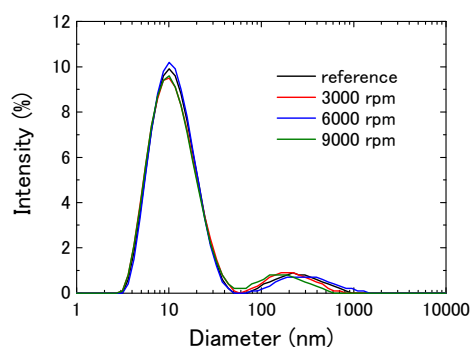


Fig. 4. Diameter distribution of pure silica zeolite films after hydrothermal synthesis was measured with dynamic light scattering.

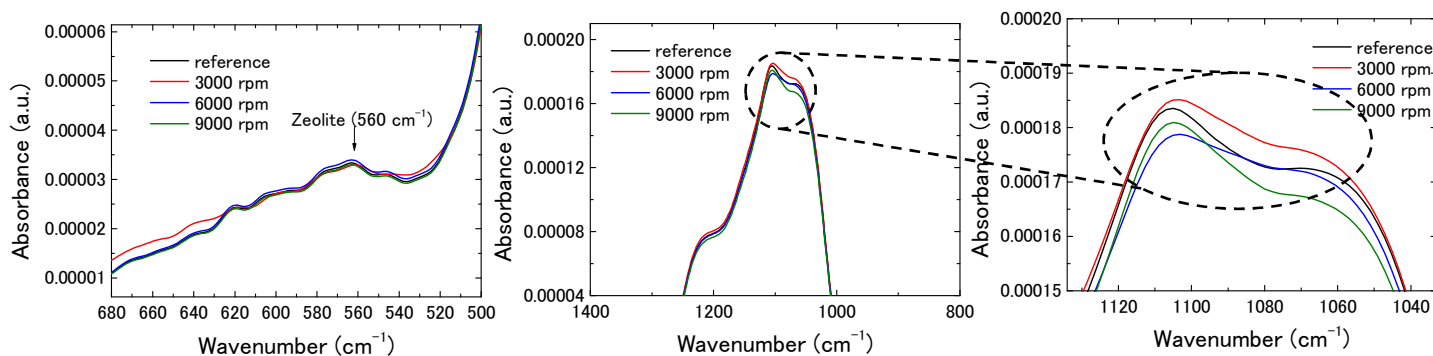


Fig. 5. Fourier transform infrared spectra of pure silica zeolite films. (a) Zeolite peak at 560 cm⁻¹. (b),(c) The network Si-O-Si bond at 1000-1250 cm⁻¹.

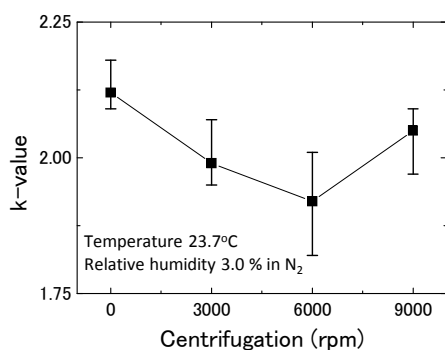


Fig. 6. Dielectric constants of pure silica zeolite films for each centrifugation.

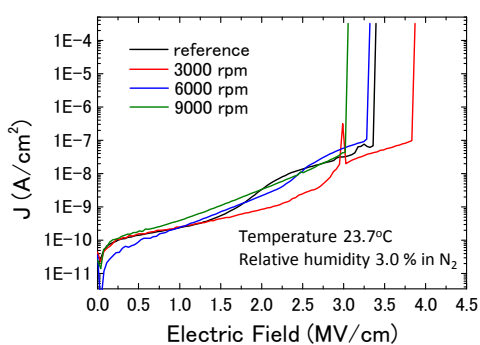


Fig. 7. Leakage current density of pure silica zeolite films for each centrifugation.

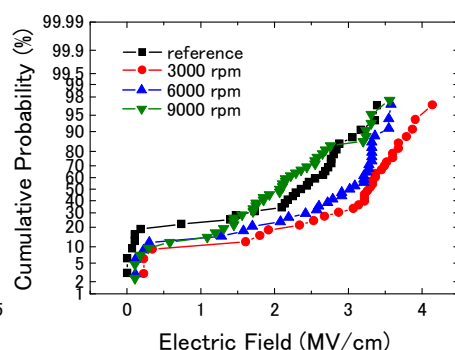


Fig. 9. Weibull plot of breakdown field strength.