

Layered Low-k Porous Silica Zeolite Films for Inter-Metal Dielectrics with High Elastic Modulus

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1. Introduction

With the rapid development of ultra large scale integrated circuit (ULSI), the signal delay time increases due to the increase of interconnect resistance and parasitic capacitance. To overcome this problem, low dielectric constant (low-k) interlayer dielectric films are needed. Mesopores have been introduced into the low-k materials to reduce its capacitance. However, the mechanical strength of the low-k film with mesopores becomes lower, and the lower mechanical strength has been inducing some critical problems of ULSI integration, e.g., CMP failure. The low-k films with strong mechanical strength are required. Low-k porous silica films with zeolite have been suggested for higher mechanical strength [1-3]. Zeolite is one of oxide crystal and strengthens the mechanical strength of the low-k films.

In this paper, three-layered structure of porous silica film derived from zeolite particles was investigated for high mechanical strength and reliability.

2. Experimental

The MEL type zeolite was synthesized by the process flow as shown in Fig. 1. Tetrabutyl ammonium hydroxide (TBAOH), tetraethyl orthosilicate (TEOS), ethyl alcohol and DI water were mixed, and heated in autoclave for 48 hours at 60°C to make precursor. The precursor was then cooled down to room temperature, and heated again at 80°C for 120 hours. After butanol and the surfactant Brij78 were added to the suspension, the film was formed by spin coating on a Si wafer, and calcined in nitrogen ambient for 5h at 400°C. The film was then annealed in the tetramethylcyclotetrasiloxane (TMCTS) atmosphere at 350°C. UV light of wavelength 172 nm was irradiated to help the removal of surfactant. Film damages at the UV irradiation process were cured by the annealing TMCTS ambient at 350°C. In order to measure electrical characteristics, aluminum electrode was deposited by using the vacuum evaporation system.

3. Results and Discussion

Figure 2 shows the Fourier-transform infrared (FT-IR) absorption spectra of pure silica zeolite and porous silica films. In the spectra of synthesis temperature 80°C and 100°C, the peak absorbance of the zeolite crystal is observed at 560 cm⁻¹. Pore size distributions are obtained from the small angle X-ray diffuse scattering spectroscopy is shown in Fig. 3. The pore sizes are 3.60, 3.05 and 2.95

nm for the 1, 2 and 3-layered films, respectively. Figure 4 shows refractive indices and porosities of the layered structure film. These refractive indices were measured by spectroscopic ellipsometry. The porosity x was calculated by using Lorentz-Lorentz relation:

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

where n and n_{SiO_2} are refractive indices of dielectric film and SiO₂, respectively. As number of the layers increased, porosity of the film decreased. Figure 5 shows the FT-IR absorption spectra of the layered structure films. Si-OH peak at 3743 cm⁻¹ was not observed, so that hydrophobic films were formed. Fig. 6 shows densities of the layered low-k films. These densities were measured and analyzed by the small angle X-ray scattering spectroscopy (SAXS). As the layer increases, the density of the low-k increased. Figure 7 shows the relation of elastic modulus and dielectric constants. The elastic modulus and dielectric constants also increased as number of layer increases. The elastic modulus increases to 20% as 7% increase of dielectric constant. In this multi-layer low-k spin-coating method, pores are formed and restricted inside each layer against conventional one, and there were no pores on the layer's interface, so that elastic modulus increased. Figure 8 shows the leakage current characteristic of the layered-structure film. The leakage current decreased as the number of layer increases.

4. Conclusions

The three-layered low-k porous silica zeolite film was investigated for high mechanical strength and reliability. As number of layers increase, the elastic modulus increased and the leakage current decreased. Pores were formed and restricted inside each layer, and pores did not exist on the layer's interface, so that elastic modulus increased. The elastic modulus increased about 9 GPa in the three layered film. This Low-k technology with high elastic modulus and low leakage current is advantageous to integrate 22nm-node ULSIs and beyond.

References

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- [3] C-T. Tsai et al., Thin Solid Film **517**(6), 2039 (2009).

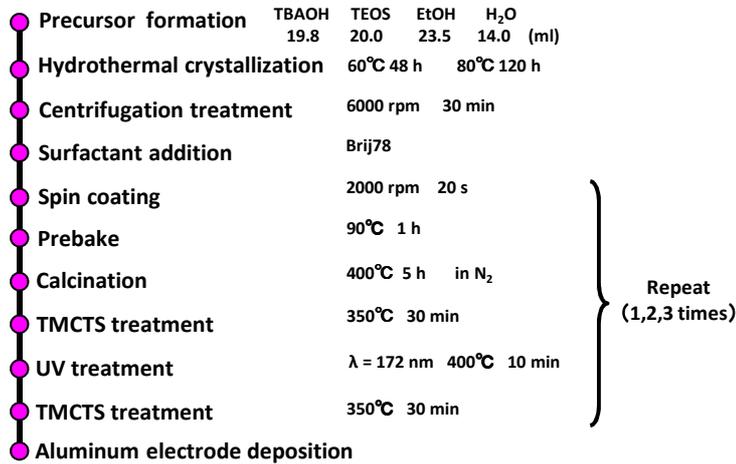


Fig.1. Process flow of pure silica zeolite film formation.

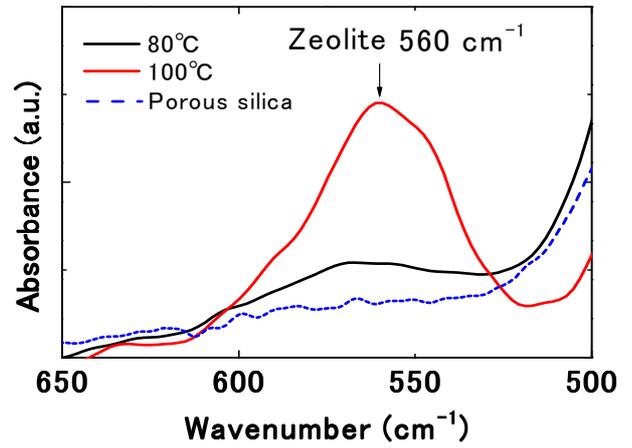


Fig. 2. Fourier transform infrared spectra of pure silica zeolite and porous silica films.

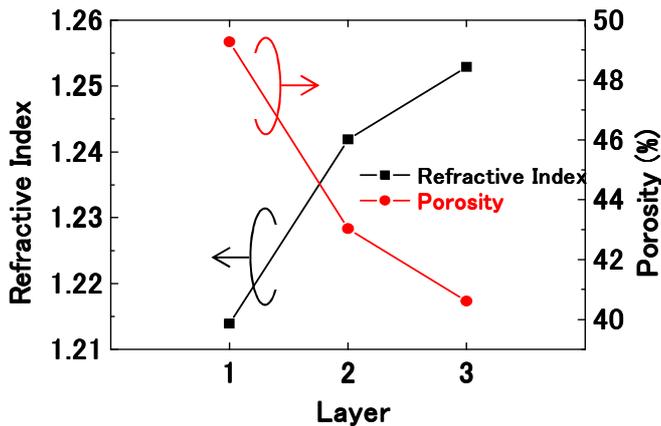


Fig. 3. Refractive indices and porosity of the layered structure pure silica zeolite films.

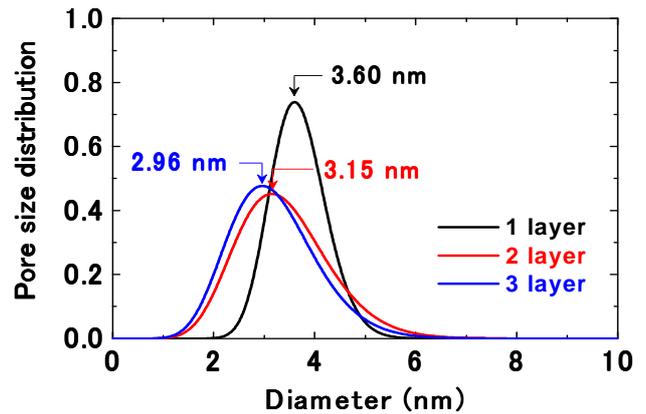


Fig. 4. Pore size distribution of the layered structure pure silica zeolite films.

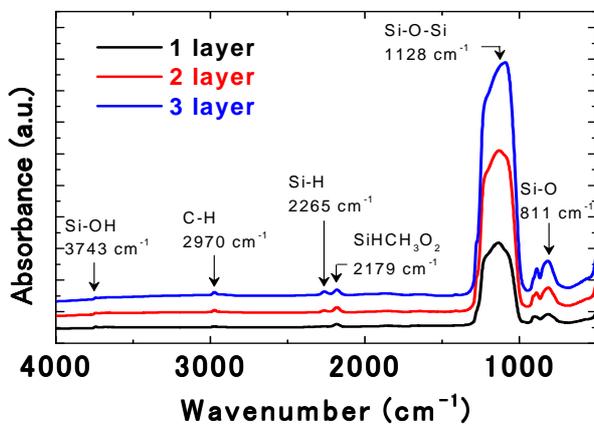


Fig. 5. Fourier transform infrared spectra of the layered structure pure silica zeolite films.

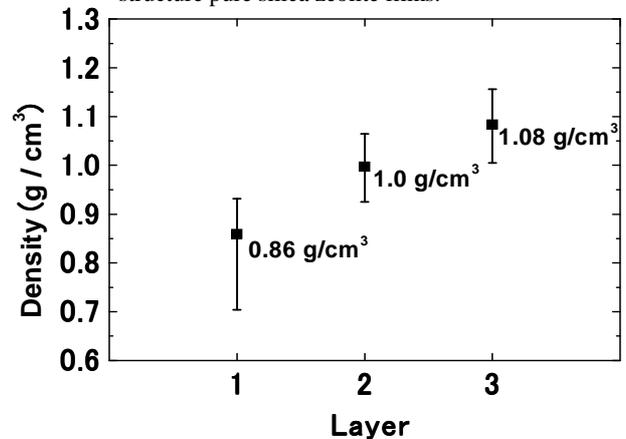


Fig. 6. Density of the layered structure pure silica zeolite films as a function of number of layers.

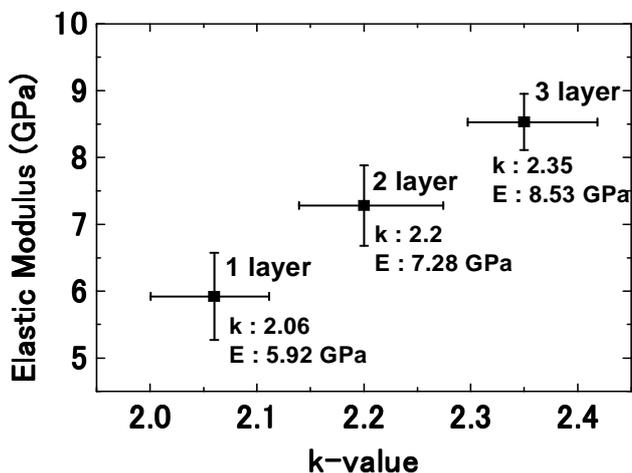


Fig. 7. The relation of elastic modulus and dielectric constants of the layered structure films.

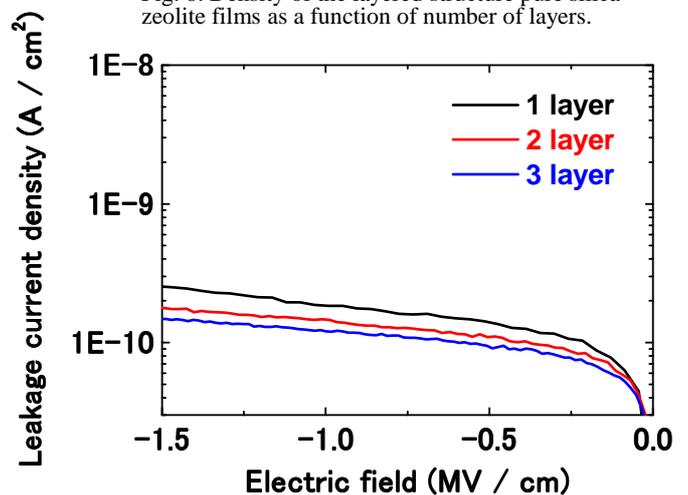


Fig. 8. Leakage current versus electric field of the layered pure silica zeolite structure films.