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Vapor Phase Silylation Hardening Process for Porous Silica Low-k Films

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1. Introduction

Porous silica is a promising candidate for low dielectric constant (low-k) materials. However, it has low mechanical strength and low moisture-proof. In order to improve these properties, silylation hardening treatment using TMCTS (1,3,5,7-tetramethylcycrotetrasiloxane) has been developed. TMCTS has methyl groups which make pore surface hydrophobic. Furthermore, TMCTS forms cross-linked polymer on the pore surface wall and reinforces porous silica film [1]. In this work, the effects of silylation treatment with TMCTS on the porous silica films are investigated. Especially, highly efficient reaction furnace for TMCTS is developed.

2. Experimental

Figure 1 shows the preparation procedure, which consists of a sol-gel technique based on the self-assembling of surfactant templates [2]. A precursor solution was prepared by the mixture of silica precursor of 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 prebaked at 90˚C for 1 hour under air ambient and calcined at 400˚C for 5 hours in dry air. A heating rate of 1˚C/min was adopted.

Then silylation treatment with TMCTS for the porous silica film was carried out at 350˚C under nitrogen ambient. Figure 2 shows a schematic diagram of a TMCTS silylation furnace. First, the reaction furnace was purged with nitrogen. Next a substrate was heated at 350˚C. Then the bubbling tank which contains TMCTS liquid was heated at 65˚C. Finally, nitrogen was flowed to the reaction furnace through the bubbling tank, TMCTS vapor was transported to the reaction furnace. After TMCTS treatment the reaction furnace was cooled down for 1 hour.

In order to measure the electrical properties, a MIS capacitor was fabricated by direct current magnetron sputtering. The leakage current and capacitance versus voltage measurements are carried out after 200˚C baking for 10 hours in nitrogen ambient environment with 2.0% RH in order to remove water in the films. Figure 3 shows possible mechanism for TMCTS reaction on porous silica wall surface. First, a part of Si-H groups of TMCTS reacted with Si-OH groups on the porous silica wall surface via dehydrogenation (Fig. 3a). Then, TMCTS molecules polymerized after silylation via hydroxylation of residual Si-H groups, followed by the reaction with Si-OH groups (Figs. 3b and c). Finally polymerized TMCTS network was formed on porous silica wall surface (Fig. 3d)[1].

3. Results and Discussion

Figure 4 shows TMCTS treatment time dependence of porosity. Porosity was calculated from the refractive index measured by ellipsometry. Porosity increased then decreased as TMCTS treatment time increased.

FTIR absorption spectra of the porous silica with several TMCTS treatment times are shown in Figs. 5 and 6 in the range of 2000-4000cm^{-1} and 950-1350cm^{-1}. As shown in Fig. 5, 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, and the absorption peak at 2970cm^{-1} related to the C-H bond and the absorption peak at 2183cm^{-1} related to the H-SiCH_3O_2 bond increased by the TMCTS treatment. These indicate that porous silica film became hydrophobic. As shown in Figs. 5 and 6, the absorption peak at 1275cm^{-1} related to the H_3C-SiO_3 bond and the absorption peak at 2258cm^{-1} related to the H-SiO_3 bond increased by the TMCTS treatment. This indicates that TMCTS formed polymers on the porous silica wall surface.

Figures 7 and 8 show the leakage current and the dielectric constant of porous silica films as a function of TMCTS treatment time, respectively. The leakage current decreased to the order of 10^{-9} (A/cm^2) for more than 1 min of TMCTS treatment. The suppression of leakage current is attributed to the reduction of OH-related absorption, resulting in dramatic decrease of an ionic current component. The dielectric constant decreased by TMCTS treatment in 2 min. The variation of k-value is also consistent with the reduction of OH-related absorption after TMCTS treatment. K-value increased after 4 min and 8 min. This is attributed to the decrease of the porosity.

4. Summary

The time dependency of vapor phase TMCTS treatment for the porous silica films was investigated. After 1 min of TMCTS treatment, the absorption of TMCTS and cross-link of TMCTS and resulting hydrophobicity of porous silica films were confirmed by FTIR. The leakage current density decreased to the order of 10^{-9} (A/cm^2) for more than 1 min of TMCTS treatment and the dielectric constant was reduced to about 75% after 2 min of TMCTS treatment. Consequently, the TMCTS treatment for the porous silica films was accomplished in 2 minutes.

References

[1] K. Kohmura, et al., Thin Solid Films 515 (2007) 5019-5024.
[2] K. Kohmura, et al., Mat. Res. Soc. Symm. Proc. 863 (2005) B3. 10. 1.

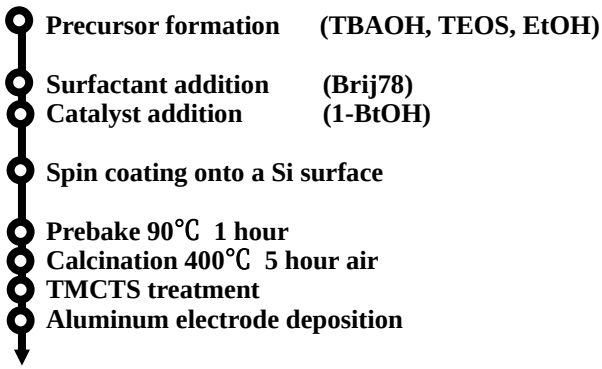

Fig. 1. Process flow of porous silica film formation

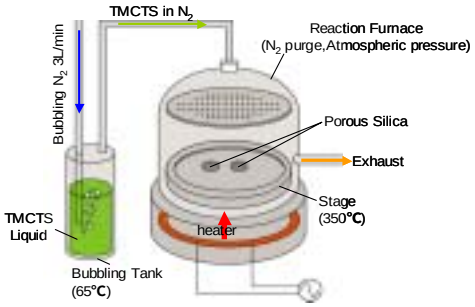

Fig. 2. Schematic diagram of a TMCTS annealing furnace

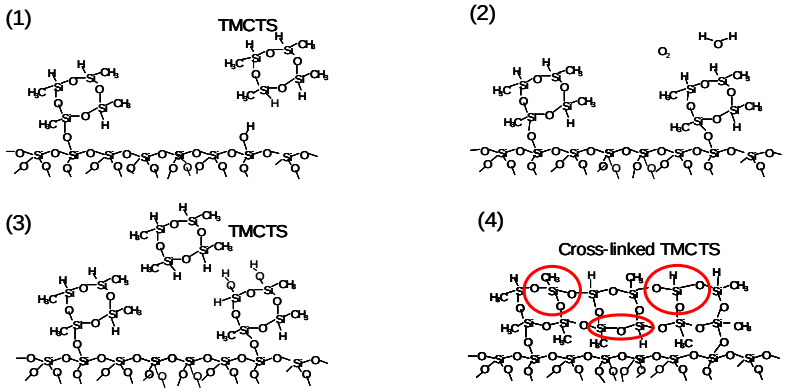

Fig. 3. Possible mechanism for TMCTS reaction on porous silica wall surface

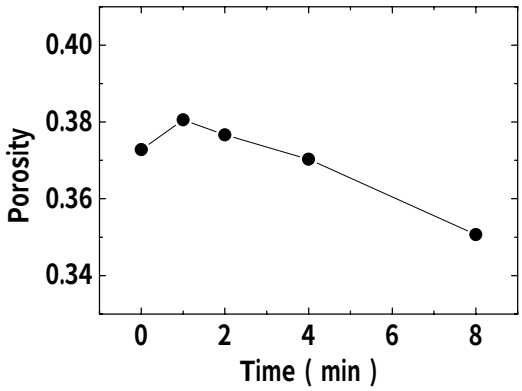

Fig. 4. Porosity versus TMCTS treatment time

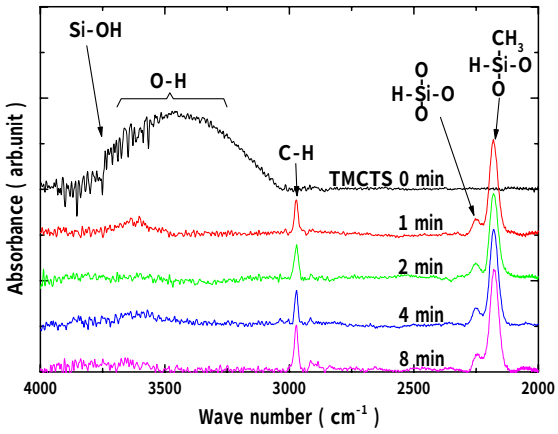

Fig. 5. FTIR spectra, in the range of 2000-4000cm^{-1}

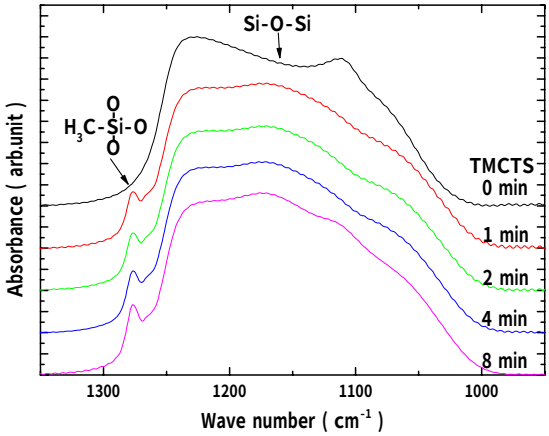

Fig. 6. FTIR spectra, in the range of 950-1350cm^{-1}

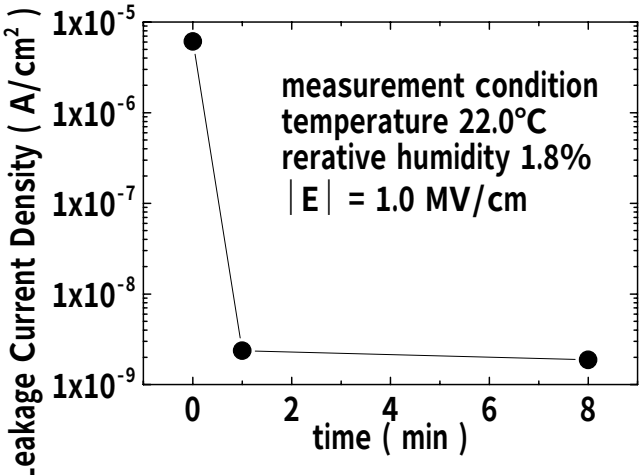

Fig. 7. Leakage current density as a function of TMCTS treatment time

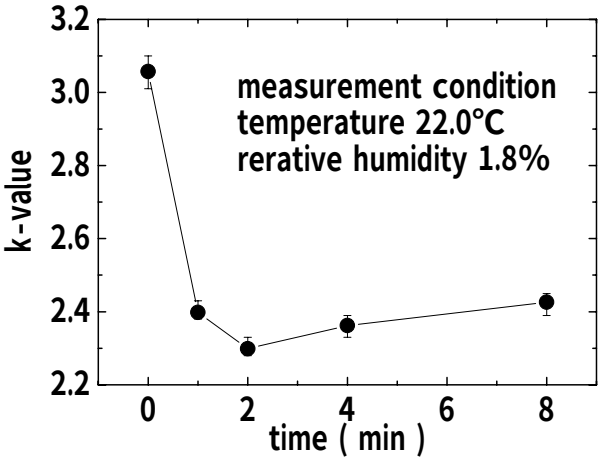

Fig. 8. k-value as a function of TMCTS treatment time