

**B-2-3****Effect of TEOS treatment on the properties of periodic nanoporous silica low-k film**

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**1. Introduction**

Development of ultra low-k ( $k < 2.0$ ) material is much more difficult than expected. This difficulty mainly stems from introduction of pores (air) into intermetal and interlayer dielectric thin films, though there are any other reasons. It is essentially inevitable to introduce pores into the dielectric material, or lower the film density, in order to attain the film with the dielectric constant less than 2.0. It is noted, however, that making the dielectric film porous causes the degradation of mechanical properties of the film. Conventional pore formation techniques introduce so poly-dispersed and inhomogeneous pores as to induce the association and agglomeration of pores. As a result, the film with aggregation of pores locally possesses deteriorated mechanical properties. Therefore, technologies to array the homogeneous pores in order become increasingly more important. Among others, the self-assembly technique where the surfactant assembly is applied as template offers the periodic nanoporous silica [1-8]. The periodic porous silica is considered to be promising as ultra low-k. In addition, this film is prepared simply by spin coating and sequential calcination. One of the greatest problems is, however, the thermal stability of periodic porous structure. The periodic porous silica developed so far causes a severe structural shrinkage (10~30%) by calcination [2,3,7]. Consequently, both the porosity and the mechanical strength of the film can lower.

We have developed a novel process including a vapor-phase TEOS treatment to prepare the periodic nanoporous silica film with high structural stability [9,10]. In this paper we investigate the TEOS-treated periodic nanoporous silica and discuss the mechanism for enhancement of structural stability based on the obtained properties.

**2. Experimental**

Periodic nanoporous silicate glass thin films were spun at 2000-6000rpm on a p-type Si (100) substrate or a Pt/SiO<sub>2</sub>/Si (100) substrate by a sol-gel process from TEOS, cationic surfactant, acid catalyst and solvent (water, alcohol) at RT. The spun-on films were all dried, and partly vapor-phase TEOS-treated at elevated temperatures. For reference, only thermal treatment (without TEOS vapor) was

employed. All the sample films were annealed at 673 K in air. A part of calcinated sample was silylated by vapor-phase trimethylchlorosilane (TMCS) treatment. The calcinated films were characterized as follows: the periodic structure was identified by X-ray diffraction (XRD) in  $\theta$ - $2\theta$  scan mode, the chemical bonding state was analyzed by fourier-transform infrared (FTIR) spectroscopy, the porous structure was directly observed by scanning transmittance electron microscopy (STEM), and the electrical properties (IV/CV) were measured by mercury probe method with MIS (Hg/porous silica/p-Si) structure.

**3. Results and Discussion**

Figure 1 shows a series of XRD profiles of TEOS-treated nanoporous silica on a Si substrate. This was spun at 2000 rpm. All intense diffraction peaks for (100) reflection are positioned around at  $2\theta = 2.3$  degree. Second diffraction peaks for (200) reflection were all positioned around at  $2\theta = 4.6$  degree. Typical data of evolutionary change of  $d_{(100)}$  space of periodic nanoporous silica film are summarized in Table I in order to estimate the effect of TEOS treatment quantitatively. The structural shrinkage due to calcination is evaluated to be about 1% for TEOS-treated sample. This result means that TEOS treatment prior to calcination strengthens the periodic nanoporous structure. To estimate the difference in periodic porous structure between the untreated sample and the TEOS-treated one in more detail, we adopted STEM observation. Figure 2 shows STEM images of untreated periodic nanoporous silica film and TEOS-treated one. Apparently, the structural distortion in a direction perpendicular to substrate was improved by TEOS treatment. These images correspond well to the XRD analysis. To elucidate what is essential in the reinforcement of porous structure, the thermal process (at 408 K) without TEOS was also employed prior to calcination. Figure 3 shows evolutionary changes of  $d_{(100)}$  spaces and  $\Delta 2\theta$  obtained for untreated, thermally treated and TEOS-treated sample film. TEOS treatment scarcely changes  $d_{(100)}$  space and  $\Delta 2\theta$  after calcination. On the other hand, the thermally-treated sample exhibits large  $d_{(100)}$  space decrease and  $\Delta 2\theta$  increase, as well as the untreated one. That is, periodic nanoporous structure collapses by calcination without TEOS treatment. This means that only the thermal effect can not improve the

structural stability. From another experiment, it is found that nanopores do not shrink by TEOS treatment [9]. Furthermore, FTIR spectroscopic data show that the absorption band assigned to silanol group disappears by TEOS treatment (the spectra is not shown here). We consider that TEOS molecule diffusing into porous silica wall reacts with existing silanol group and prevent periodic porous silica from structural contraction during calcination.

#### 4. Conclusions

Enhancement effect of vapor-phase TEOS treatment on the structural stability of periodic nanoporous silica film has been investigated. The TEOS treatment can suppress the shrinkage of the film during thermal treatment so that the d-spacing and the pore size of the periodic structure are kept constant after processing. The TEOS treatment enhances the structural stability, resulting in achieving reinforcement of ultra-low-k films. The mechanisms of reinforcement are penetration of TEOS molecules into the porous silica wall and reaction with unreacted silanol group, resulting in the crosslinking of silica network.

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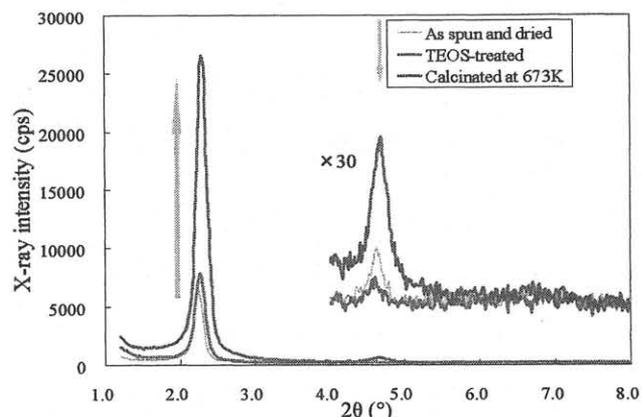


Fig. 1 XRD profile of TEOS-treated nanoporous silica films on a Si substrate.

Table I Evolution of  $d_{(100)}$  space of periodic nanoporous silica with and without TEOS treatment.

Sub	TEOS treat	$d_{(100)}$ space (nm)			Shrinkage (%)
		As-depo and dried	TEOS treated	Calcinated	
Si	w/o	4.01	-	3.11	22.5
	w/	3.37	3.29	3.22	2.2
Pt	w/o	3.65	-	2.87	21.4
	w/	3.91	3.87	3.84	0.9

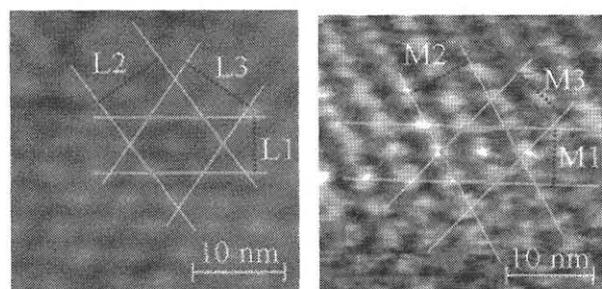


Fig. 2 Cross-sectional STEM images of untreated periodic nanoporous silica film (left) and TEOS-treated one (right). Both were prepared on Pt/SiO<sub>2</sub>/Si substrates.

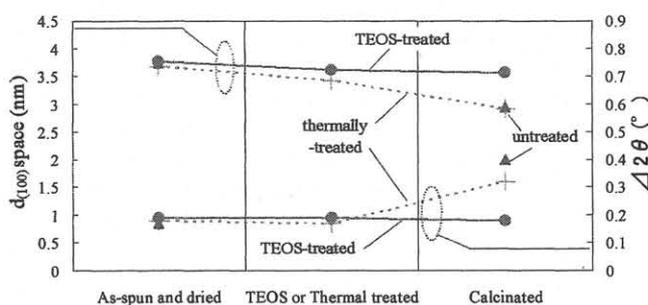


Fig. 3 Evolutional changes of  $d_{(100)}$  spaces and  $\Delta 2\theta$  (FWHM) obtained for (a) untreated, (b) thermally-treated, and (c) TEOS-treated sample film prepared on Si substrates.