

Characteristics of Self-Assembled Ultra-Low- k Porous Silica Films

Y. Oku¹, N. Fujii¹, K. Kohmura¹, K. Yamada¹, N. Hata², Y. Seino², R. Ichikawa², N. Nishiyama³, S. Tanaka³, H. Miyoshi¹, S. Oike¹, H. Tanaka¹, S. Takada², C. Negoro², A. Nakano¹, T. Ogata¹, T. Goto¹, Y. Sonoda¹, A. Ishikawa¹, T. Yoshino², H. Matsuo¹, K. Kinoshita¹, K. Ueyama³, and T. Kikkawa^{2,4}
¹MIRAI-ASET, ²MIRAI-ASRC-AIST
³Osaka University, ⁴RCNS, Hiroshima University
^{1,2}16-1, Onogawa, Tsukuba 305-8569, Japan
³1-3, Machikaneyama-cho, Toyonaka 560-8531, Japan
⁴1-4-2, Kagamiyama, Higashi-Hiroshima 739-8527, Japan

1. Introduction

Introduction of nanoscale pores (air) in the dielectric film is an efficient way to produce ultra-low- k films ($k < 2.5$). The conventional technique for pore introduction by use of progen, however, causes the agglomeration and the interconnection of pores, which degrade the mechanical properties of porous low- k films with increasing porosity.

To solve this pore agglomeration problem, we have focused on the formation of a homogeneous porous structure with a narrow pore size distribution by employing surfactant self-assembly technologies (1-5). We can prepare two types of porous silica films: One has a periodic porous structure and the other has a disordered (nonperiodic) porous structure. The periodic porous silica developed so far caused severe shrinkage of the $d_{(100)}$ spacing by calcination. To suppress such shrinkage of hexagonally ordered pore structures, we have developed the vapor-phase tetraethoxysilane (TEOS) treatment before calcination to stabilize the porous structure (2, 3). We can control the pore size distribution by changing the alkyl chain length of the surfactant (3, 4). To solve the degradation of mechanical strength by increasing porosity, we have developed the vapor-phase tetramethyl-cyclo-tetra-siloxane (TMCTS) treatment after calcination to reinforce the modulus of the skeletal silica wall, independently of the dielectric constant of the porous silica film (5).

We will report on a novel ultra-low- k porous silica film formation technology, such as self-assembling of surfactant with an acidic silica derived from TEOS, the pore size control, and the skeletal silica reinforcement.

2. Experimental

General experimental procedures are as follows: Various types of precursor solutions are adequately prepared for the desired porous silica using cationic or nonionic surfactants as self-assembled pore templates, TEOS or TEOS-derivative as skeletal silica wall, acid catalyst as a cross-linking promoter, and solvent. The prepared precursor solution is spin-coated on the substrate, dried, and calcined at an elevated temperature. The produced ultra-low- k porous silica films are characterized in terms of film thickness, refractive index, macroscopic and microscopic pore structure, chemical bonding states, electronic properties (dielectric constant and leakage current), and mechanical properties (elastic modulus, hardness, and adhesion energy).

3. Results and Discussion

In Fig. 1, the dielectric constant (k -value) and the refractive index of the periodic porous silica films are plotted as a function of the number of carbon atoms in the alkyl chain of surfactant. From this figure, it is found that

the k -value and refractive index decrease with increasing the length of the alkyl chain of surfactant. Furthermore, it is also found that the TEOS treatment before calcination is effective to lower the k -value and refractive index. Figure 2 shows the elastic modulus (E) and hardness (H) versus k -value. The effect of TMCTS treatment on the reinforcement of disordered porous silica is clearly demonstrated. It should be noted that the TMCTS treatment can increase E and H values independently of k -value.

4. Conclusions

We have developed novel ultra-low- k porous silica by use of a surfactant self-assembly technology. To lower the dielectric constant, we have developed the pore size control technologies by the TEOS treatment to stabilize the porous structure and by employing the different alkyl chains of surfactant. The mechanical properties of the porous silica films can be reinforced independently of the dielectric constant by the TMCTS treatment.

Acknowledgement

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References

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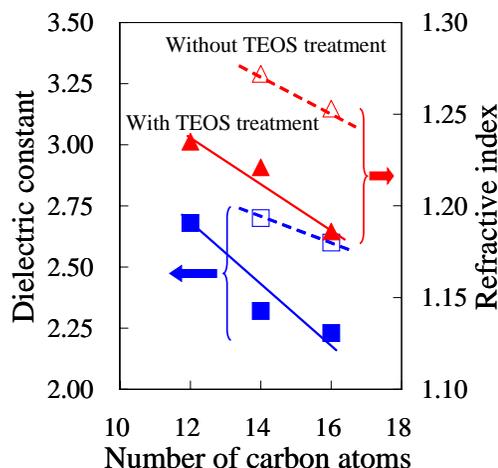


Figure 1 Dielectric constants and refractive indexes of periodic porous silica films as a function of the number of carbon atoms in alkyl chain of surfactant. Solid and open symbols represent with and without TEOS treatment, respectively.

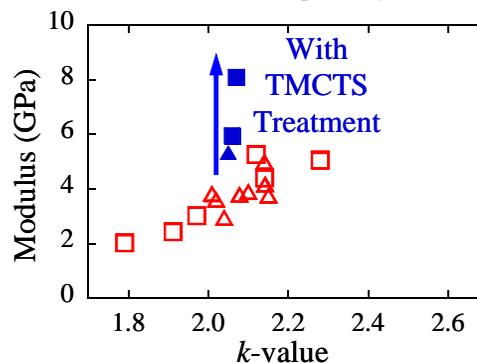


Figure 2 Elastic modulus versus k -value for disordered porous silica low- k with or without TMCTS treatment.