

## Influences of Skeletal Structure and Porosity on Dielectric and Mechanical Properties of Porous Organosilica Low- $k$ Films

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### 1. Introduction

In the development of porous low dielectric constant (low- $k$ ) insulator materials, a systematic study of material characteristics is important to clarify the effects of skeletal structure and porosity  $P$  separately on mechanical, chemical, thermal and electric properties. An earlier theoretical modeling on mechanical strength of porous silica low- $k$  films suggested the importance of improvement of skeletal strength [1, 2]. We have already reported that mechanical strength of skeletal in porous silica films correlated with ionic component of skeletal [3]. In this study, we carried out Fourier transform infrared (FTIR) spectroscopy on series of self-assembled porous organosilica (Po-SiOCH) films with wide-range of skeletal structures and  $P$  to systematically evaluate the effects of skeletal structure and  $P$ .

### 2. Experiment

Po-SiOCH films were prepared from precursor solutions of cationic cetyltrimethylammonium chloride and an acidic silica sol derived from tetraethylorthosilicate (TEOS) and dimethyldiethoxysilane (DMDEOS) by spin-coating, drying and curing. The volume ratio of DMDEOS/(TEOS+DMDEOS) and the mole ratio of surfactant/Si in precursor solution were varied from 0 to 0.25 and from 0 to 0.2, respectively.

An FTIR spectrometer with grid polarizer in dry nitrogen flow was used to record infrared transmittance. Infrared complex dielectric function was obtained by regression analysis of the spectra with an optical model [4]. UV-visible spectroscopic ellipsometry was employed to measure the thickness and refractive index. Young's elastic modulus  $E$  was measured by an MTS Systems Nano-Indenter XP with a Berkovich diamond tip.

### 3. Results and discussion

Figure 1 shows absorption spectra between 2500 and 4000  $\text{cm}^{-1}$  of Po-SiOCH films. The peaks at 2970 and 3742  $\text{cm}^{-1}$  are attributed to the  $\text{CH}_3$  asymmetric stretching (AS) vibration and OH stretching vibration, respectively. The chemical composition,  $x$ ,  $y$ , and  $z$  of  $\text{SiO}_x(\text{OH})_y(\text{CH}_3)_z$ , of samples was measured by  $^{29}\text{Si}$  MAS NMR [5]. The peak amplitude of the  $\text{CH}_3$  AS vibration shown in Fig. 2 exhibits a good correlation with the  $z$  value. The value of methyl group in skeletal monotonously increased with the increase in the DMDEOS content; consequently peak height of hydroxyl group decreased (Fig. 1) and contact angle of water to film increased (Fig. 2). These results verify that the concentration of methyl group in skeletal Si-O-Si

network can be systematically controlled by the ratio of DMDEOS in precursor and quantitatively evaluated by FTIR spectra as shown in Fig. 2.

Figure 3 shows an example of the obtained infrared complex dielectric function  $\epsilon$  of Po-SiOCH film by regression analysis. Real part of  $\epsilon$ ,  $\text{Re}(\epsilon)$ , at the highest end of the wavenumber  $\epsilon_\infty$  is dominated by the contribution of electronic polarization, while  $\text{Re}(\epsilon)$  at the lowest end of the wavenumber  $\epsilon_0$  carries contributions not only from electronic but also from ionic polarization associated with mid-infrared absorption bands analyzed in the present study. Solid curves in Fig. 3 show the complex dielectric function of skeletal  $\epsilon^{\text{skeletal}}$ , which correlates with the mechanical strength, extracted from measured  $\epsilon$  of the porous film by using Bruggeman's effective medium approximation [3].

Figure 4 (a) shows dependences of  $\epsilon_0$  and  $\epsilon_\infty$  on stoichiometric ratio of methyl function group of Po-SiOCH films. The  $\epsilon_0$  decreased abruptly with the  $z$  value in skeletal up to 0.25, while the  $\epsilon_\infty$  stayed almost constant. This change is caused by the decrease in the ionic polarization with the increase in methyl group. Unlike the change of  $\epsilon_0$ , the  $E$  value monotonously decreased from 10 to 3 GPa with the ratio of methyl group as shown in Fig. 4 (b).

Figure 5 shows dependences of dielectric properties and  $P$  on mole ratio of surfactant/Si for Po-SiOCH films with DMDEOS/(TEOS+DMDEOS) = 0.20. The  $\epsilon_0$  value was decreased from 2.73 to 1.95 with increasing of surfactant concentration. This change is caused by decrease in both ionic and electronic polarization with the increasing of  $P$ , as shown in the inset of Fig. 5. The dielectric property of SiOCH films can be controlled by both the ratio of DMDEOS/(TEOS+DMDEOS) and the ratio of surfactant/Si in precursor solution.

Figure 6 shows dependence of  $E$  on  $P$  and ionic component of skeletal ( $\epsilon_0^{\text{skeletal}} - \epsilon_\infty^{\text{skeletal}}$ ), as shown in Fig. 3) in porous and nonporous SiOCH films. With increasing of  $P$  and/or decreasing of ionic component of skeletal,  $E$  of films decreased. The decrease of ionic component in skeletal can be interpreted as a degradation of cross-linking density of skeletal with increasing methyl group, which results in the deteriorated mechanical strength of Po-SiOCH films. The overall  $E$  of Po-SiOCH films depends on both  $E$  of skeletal and  $P$ . The  $E$  of skeletal in Po-SiOCH is evaluated by ionic component of skeletal.

### 4. Conclusions

Self-assembled Po-SiOCH low- $k$  films with a wide-range concentration of methyl group in skeletal have been prepared by varying the DMDEOS concentration in TEOS based precursor solution. Though improvement of the

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hydrophobicity and reduction in the dielectric constant are achieved by high concentration of DMDEOS in the precursor solution, the superfluous addition leads to the degradation of the mechanical strength as a decrease of cross-linking density of skeletal. We have obtained a correlation among  $P$ , ionic component of skeletal and  $E$ . This correlation enables us to distinguish the  $E$  of skeletal from the overall  $E$  of Po-SiOCH films. For achieving both higher  $E$  and lower  $k$  value, it is important to control skeletal structures by optimizing concentration of methyl group.

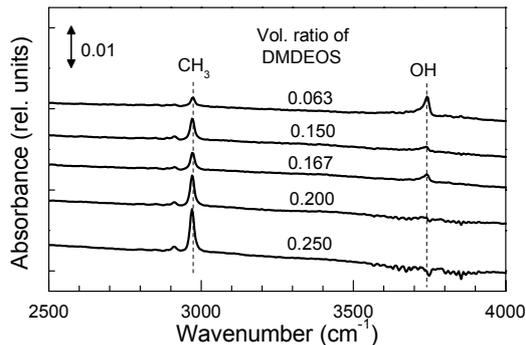


Fig. 1 Absorption spectra of porous organosilica low- $k$  films. The curves are arbitrarily shifted in the vertical direction.

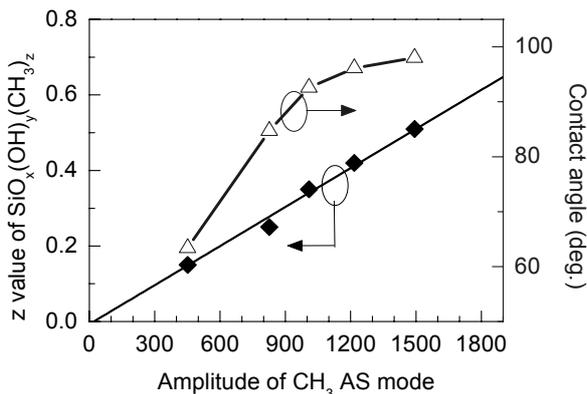


Fig. 2 Integrated area of  $\text{CH}_3$  AS vibration mode against stoichiometric ratio of methyl group and contact angle of water.

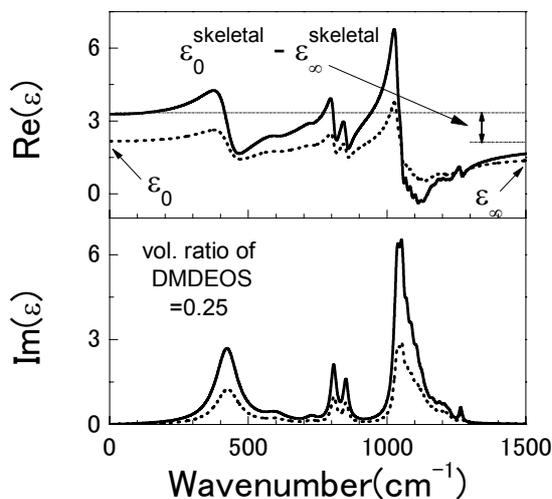


Fig. 3 Infrared complex dielectric function of Po-SiOCH film with  $\text{DMDEOS}/(\text{TEOS}+\text{DMDEOS})=0.25$ . Dotted and solid curves are the spectra of the overall porous film and of skeleton only.

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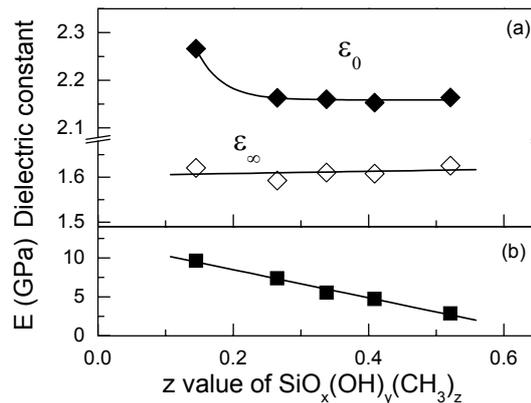


Fig. 4 Dependences of dielectric constant,  $\epsilon_0$  and  $\epsilon_\infty$ , (a) and  $E$  (b) on stoichiometric ratio of methyl group of Po-SiOCH films.

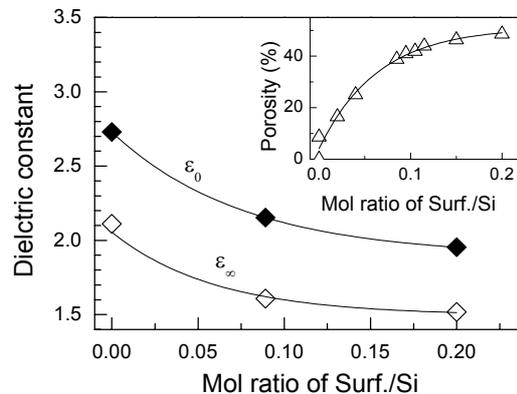


Fig. 5 Dependences of  $\epsilon_0$  and  $\epsilon_\infty$  on mole ratio of surfactant/Si for Po-SiOCH films with  $\text{DMDEOS}/(\text{TEOS}+\text{DMDEOS}) = 0.20$ . The inset is a dependence of porosity  $P$  on mole ratio.

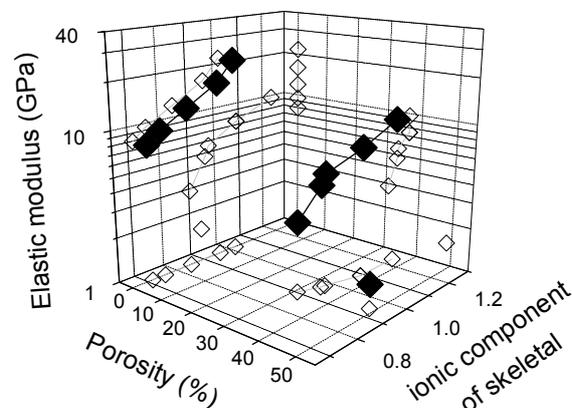


Fig. 6 Dependences of  $E$  on  $P$  and ionic component of skeletal in porous and nonporous SiOCH. Solid and open symbols show 3D and 2D views of results, respectively.