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Control of Pore Size and Porosity in Periodic Porous Silica Low-k Films

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1. Introduction

We report experimental results on pore size and lattice constant of a series of periodically ordered porous silica films prepared by varying the length of pore-generating template molecules. Control of pore size, porosity and pore geometry in porous low-k films are very important since they govern the performance, reliability, and production yield of interconnect structures. The pore structure affects the dielectric constant, its uniformity / anisotropy, moisture uptake, impurity infiltration, and other physical and chemical processes which occur during gas- and liquid-phase processes and during temperature cycles. Impurity diffusion, current leakage and dielectric breakdown mechanisms during device operation might also be affected by pore structures..

In our earlier work, we reported that lower dielectric constant and refractive index periodic porous silica films can be obtained by using longer template molecule and a greater surfactant / Si molar ratio [1]. It is the purpose of the present work to study the effects of those preparation parameters on the pore structure.

2. Experimental

The series of periodically ordered porous silica films of 300 – 400 nm in thickness were prepared by spin-coating, drying, tetraethoxysilane (TEOS) vapor treatment at 453 K, and calcinations processes at 673 K from acidic silica sol derived from TEOS solution mixed with cationic alkyltrimethylammonium chloride $C_nH_{2n+1}N(CH_3)_3Cl$ (CnTAC) surfactant template, where n denotes the number of carbon atom in the alkyl chain. Details were reported earlier [1]. For the X-ray diffraction / scattering analysis [2], we employed thin-film X-ray spectrometer (Rigaku, Model ATX-G) equipped with a 18 kW Cu Kα X-ray generator. Low-k film coated silicon substrate was mounted onto the goniometer. After calibration of X-ray and goniometer alignments, measurements were performed in $\theta - 2\theta$ configuration of out-of-plane X-ray diffraction / scattering with slit collimation, for which sample was tilted by 0.1 degree off angle $\Delta\omega$ to avoid specular X-ray reflection. An X-ray monochrometor consisting of four Germanium (220) single crystals were used for specular reflectance measurements from which the low-k film densities and thicknesses were determined.

3. Results and Discussion

Figure 1 shows the X-ray diffraction and scattering of the periodically ordered porous silica low-k films prepared with the C12TAC, C16TAC, and C18TAC surfactants, respectively. The structures observed in $2\theta < 1$ degree are related to the critical incidence angles of X-ray from air into the low-k films and then into the Si substrate. On the other hand, the prominent peaks which appear in $2.5 < 2\theta < 4.5$ degrees are due to the X-ray diffraction from the ordered periodic pore structures into the depth direction. The observed shift of the peak position toward lower 2θ angle with the alkyl chain length n indicates that the unit length of the periodic structures (d_{space}):

$$d_{space} = (\lambda / 2) / \sin\theta \qquad (1)$$

correlates with the alkyl chain length of the template. Here, λ is the wavelength 0.154 nm of the Cu Kα line X-ray. Table I summarizes these results. The increase of the diffraction peak height withan increase of n shows the higher orderliness of the periodic structure in the low-k films prepared with the template with longer alkyl chain length. The appearance of the second order diffraction peak at $2\theta = 5.62$ degrees in the spectra of the C18TAC sample also support the higher orderliness in the film.
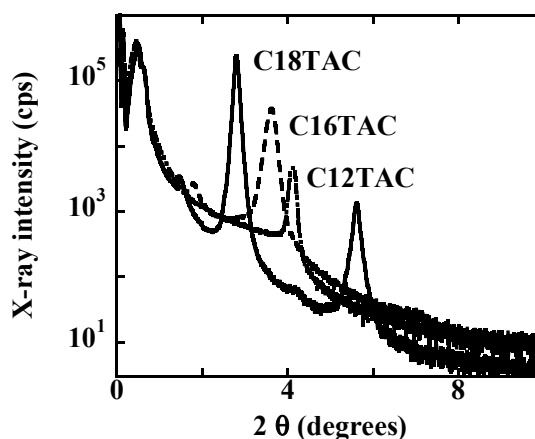

Fig. 1 X-ray diffraction / scattering spectra of periodically ordered porous silica low-k films with C12TAC (dash dotted line), C16TAC (dashed line) and C18TAC (solid line) surfactant templates, respectively.

Table 1 Dependencies of the X-ray diffraction (100) peak position and d-spacing of the periodic porous silica low-k films on the selection of surfactant molecule.

surfactant	(100) peak position	d_{space} (nm)
C12TAC	4.13	2.14
C16TAC	3.63	2.43
C18TAC	2.78	3.15

Small angle X-ray scattering from the pores appears as the baselines of the X-ray spectra in Fig. 1 in addition to the diffraction peaks. Fig. 2 illustrates the way how the X-ray scattering appearing as the baseline of the spectrum (solid line) from the sample prepared with C18TAC surfactant was fitted with the simulated X-ray scattering curve (the dashed line) [2]. Here, the horizontal axis is the scattering vector Δq:

$$\Delta q = 4 \pi \sin \theta / \lambda \quad . \tag{2}$$

By best fitting the experimental spectra with simulation results, pore size is determined. Figure 3 shows the the average of thus obtained pore size on the alkyl chain length n in the surfactant CnTAC. The slope of about 0.1 nm is reasonable because it is comparable to the molecular length increment per CH_2 chain.

Thickness of the pore wall estimated from the experimentally determined pore diameter and d-spacing turned out to be approximately constant at 0.5 nm, independent of the alkyl chain length. These results are schematically summarized in Fig. 4, where pore size is successfully controlled by varying the alkyl chain length n of the CnTAC surfactant template, while the pore wall thickness stays almost constant.
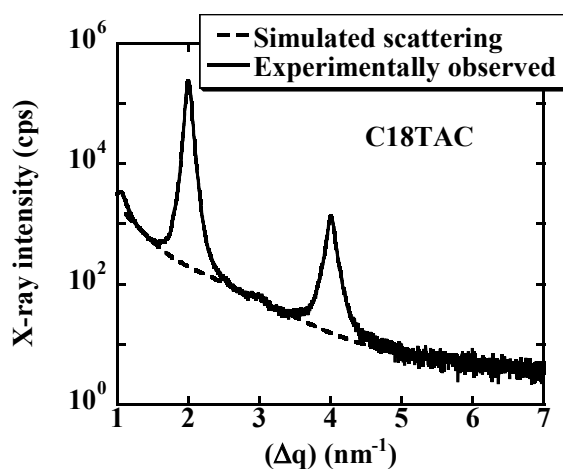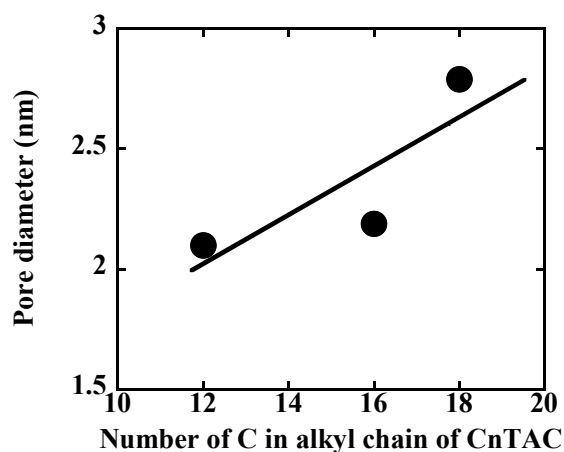

Fig. 3 Pore diameter in periodically ordered porous silica low-k films versus the number of C in alkyl chain of CnTAC surfactant used.
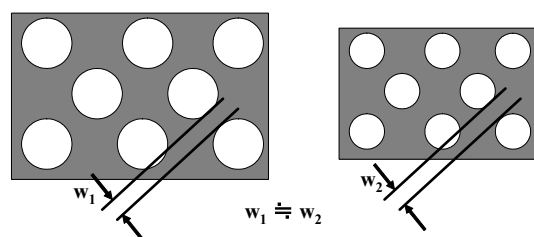

Fig. 4 A schematic model of pore-size control by the selection of surfactant template molecule by keeping the wall thickness w_i (i = 1, 2) nearly constant.

4. Conclusions

A series of periodically ordered porous silica low-k films has been studied by X-ray diffraction / scattering measurements, and a successful control of pore size by the selection of pore-generating surfactant template molecules has been demonstrated. This will give a way for control of low-k film properties which will promise the narrow process window tuning in the coming technology node, ultra low-k / Cu interconnect integration.

References

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Fig. 2 X-ray scattering / diffraction spectra plotted against the scattering vector for the low-k films.