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Structure control of periodic porous silica film for low-k application

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1. Introduction

In recent years, porous silica films with an ordered periodic pore structure have much attention as a candidate for ultra low-dielectric constant (low-k) film of copper dual-damascene interconnect technology [1-3]. Since the ordered periodic structures of silica films are formed by surfactant self assembly [4], the synthesis procedures of these films are simple, resulting in employing conventional equipments. However, there are many conditions to be optimized in the synthesis procedures of periodic silica films and their precursor solutions. In this paper, the process control of the ordered periodic pore structure is described for making low-k films with high porosity.

2. Experimental methods

Precursor solutions were prepared by adding both cationic alkyltrimethylammonium(ATMA) chloride surfactants ($CH_3(CH_2)_nN(CH_3)_3)Cl$, $C_{n+1}TACl$, n=11, 15) and an acidic silica sol prepared from tetraethylorthosilicate (TEOS) to alcohol with water. The surfactant/Si molar ratios was changed from 0.20 to 0.25. After homogeneous solutions were obtained, thin films were formed by spin coating on Si substrates. After drying, the samples were calcined to burn out the surfactants and to stabilize the structure and chemistry of the films as follows.

(i) The film was aged/dried at 453K for 1 hour, and heated slowly up to 673K in a vacuum ($<1.5x10^{-4}$ Pa) or an air atmosphere. (ii) The film was reinforced with additional silica by adsorbing ~~of~~ TEOS vapor at 453K [3]. The film was then heated up to 673k in an air atmosphere.

After calcination at 673K, all films were vapor treated with HMDS (Hexametyldisilazane) to impart hydrophobi- city to the films.

The film characterization was carried out by using a mercury C-V probe, TEM, X-ray diffraction (XRD) analysis, and ellipsometry.

3. Results and Discussions

Figure 1 shows a cross-sectional TEM photograph of the obtained silica film calcined in vacuum using $C_{16}TACl$ as a pore template. The obtained silica film had an ordered and stratified pore structure, and its period was approximately 2 nm. This is consisted with the lattice constant obtained from XRD pattern, shown in Fig.2.

Table 2 compares the values of dielectric constants, refractive index, and d-spacing of obtained porous silica films using $C_{16}TACl$ as a pore template. When surfactant/Si ratio was 0.20, the dielectric constant and refractive index were decreased with increasing d-spacing. Since the d-spacing of these films before calcination was approximately 3.6 nm, this result suggests that the pore size and porosity of porous silica films increase by suppressing the shrinkage of d-spacing during calcination process. The TEOS vapor treatment before calcination was effective to suppress the shrinkage of d-spacing, and to obtain the porous silica film with low dielectric constant and low refractive index. It is also found that the dielectric constant, refractive index, and d-spacing decrease with increasing the surfactant/Si molar ratio. The thickness of silica layer between pores might decrease with increasing the surfactant/Si ratio.

Table I Properties of periodic porous silica films using $C_{16}TACl$ as a pore template.

Sample No, Calcination process, and atmosphere	Surfactant/Si	Dielectric Constant (at 1Mhz)	Refractive Index	d-spacing (nm)
1. (i), Air	0.20	2.96	1.281	1.69
2. (i),Vacuum	0.20	2.55	1.241	2.14
3. (ii) ,Air	0.20	2.32	1.214	2.78
4. (ii), Air	0.25	2.23	1.186	2.58

Figure 3 shows the relationship between the number of carbon in alkylchain of surfactant and the d-spacing of silica film. In this case, the surfactant/Si molecular ratio was 0.25. From this figure, it is found that the d-spacing of the periodic porous silica film was successfully controlled by the length of Alkylchain of surfactant template. Figure 4 shows that the dielectric constant and refractive index of the film using $C_{16}TACl$ are lower than that of film using $C_{12}TACl$. This result suggests that the film using a long surfactant such as $C_{n+1}TACl$ (n=17, 19, 21) have ultra low dielectric constant and refractive index. Indeed, the film using $C_{18}TACl$ had large d-spacing (d=3.01nm, after calcinnation) and low refractive index (R.I= 1.161).

The d-spacing of the film using $C_{16}TACl$, calcined in air without TEOS vapor treatment (process (i)) is also plotted as a gray marker in Figs. 3 and 4. Although a long surfactant was used, the d-spacing of this sample was reduced remarkably after calcination, and similar to the value of $C_{12}TACl$ calcined with TEOS vapor treatment. Figure 4 shows that the dielectric constant and refractive index of this sample are also similar to that of the film using $C_{12}TACl$.

4. Conclusions

The porous silica films with an ordered periodic pore structure were synthesized, and the pore structures were successfully controlled by the length of ATMA surfactant molecules and calcination process. The long surfactant template molecule can be used to lower the dielectric constant and refractive index of the periodic porous silica film.

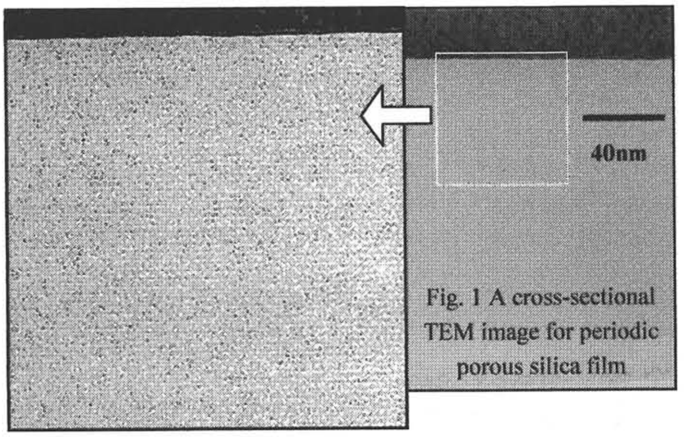

Fig. 1 A cross-sectional TEM image for periodic porous silica film

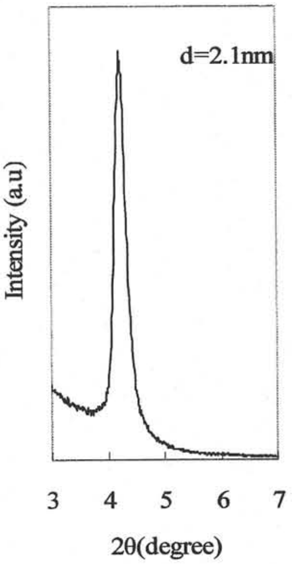

Fig.2 X-ray diffraction pattern for ordered porous silica film

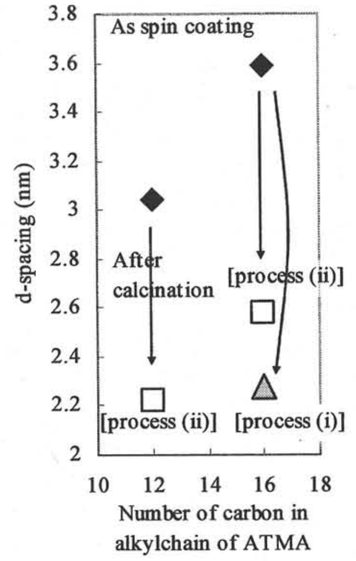

Fig.3 d-spacing of periodic porous silica film as a function of ATMA surfactant length

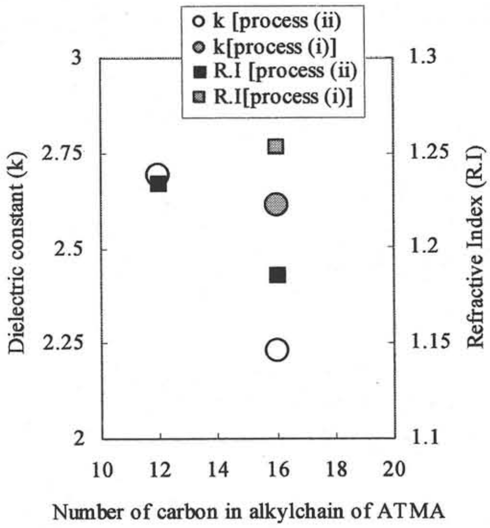

Fig.4 Dielectric constant and refractive index as a function of ATMA surfactant length

Acknowledgments

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References

[1] H.Murakami, C.Tanaka and H.Yamakawa, *Proc. Advanced Metallization Conf, P.173 (2000)*

[2] H.Fan, S.Reed, T.Baer, R.Schunk, G.P.Lopez, C.J.Brinker, *J.Microporous and Mesoporous Materials, 44-45(2001)625.*

[3] Y.Oku, N.Nishiyama, S.Tanaka, K.Ueyama, N.Hata and T.Kikkawa, *Materials Research Society Spring Meet.2002.*

[4] C.J.Brinker, Y.Lu, A.Sellinger, H.Fan, *Adv.Mater.11(1999)579.*