J. Chin. Inst. Chem. Engrs., Vol. 34, No. 2, 211-217, 2003

Low Dielectric Constant Silica Films Prepared by a Templating Method

Chih-Yuan Ting[1], Chen-An Wu[2] and Ben-Zu Wan[3]
Department of Chemical Engineering, National Taiwan University
Taipei, Taiwan 106, R.O.C.

Wen-Fa Wu[4]
National Nano Device Laboratories, National Science Council
Hsichu, Taiwan 300, R.O.C.

Abstract—The preparation of low dielectric constant porous silica films by a templating method was studied in this research. Several organic compounds (including ionic and nonionic surfactants), which can be dissolved in the coating solution, were used as the template. They were applied to make pores in the film by burning them off during calcination in the air. TEOS (tetraethyl orthosilicate) was used as the silica source for the preparation of sol-gel. The processes that influenced the film thickness and the film surface modification were investigated. It was found from this research that the concentration of TEOS in the coating solution affected the film thickness the most. The spin speed during spin coating and the temperature increasing rate during the calcination process only slightly influenced the thickness. The surface modification was most successful when the film was immersed in the HMDS (1,1,1,3,3,3-hexamethyl disilazane) and toluene solution at 80°C. Moreover, for the templates tested in this research, it was found that the film using Tween 80 (polyoxyethylene(20) sorbitan monooleatel, a non-ionic surfactant) exhibited the lowest dielectric constant.

Key Words : Low *k* materials, Porous silica, Spin coating, Thin film, Sol-gel, Dielectric constant

INTRODUCTION

As the packing density of metal lines in semiconductors continues to increase, intermetal dielectric films with $k<3$ will be required. Recently, it has been reported that porous silica is one of the promising materials to meet this requirement (Martin et al., 2000). This is because the dielectric constant of porous silica is a combination of that of air (about 1) and solid SiO_2 (3.9-4.5); therefore, by increasing the pore volume in a silica film, the k value of this material can be reduced. Porous silica films can be synthesized from TEOS (tetraethyl orthosilicate) solution. There are two methods to make the film, based on whether organic templates are used or not: (1) by an aerogel or a xerogel process (Ramos et al., 1997; Jo et al., 1997); (2) by a templating process (Yang et al., 1996; Zhao et al., 1998a; Baskaran et al., 2000; Honma et al., 2000). In the first method, the solvent extraction or other processes have to be carried out in order to make pores in the film, and the pore size in the film is hard to control. In the second method, some organic compounds are dissolved in the TEOS sol-gel. They act as templates in the film. Simply by burning off these organics in the air, the pores can be formed in the film. Therefore, films prepared in this way often possess ordered pore structures and uniform pore size. In this paper, the preparation of porous silica films by the templating process is presented. The factors controlling the film thickness and the film surface modification were studied. Moreover, several templates for making low k films were used and compared. They were TPABr (tripropylammonium bromide), $C_{14}TMABr$ (myristyltrimethylammonium bromide), $EO_{20}PO_{70}EO_{20}$ (poly (ethylene glycol)-block-poly (propylene glycol) block-poly (ethylene glycol), MW = 5800) and Tween 80 (polyoxyethylene(20) sorbitan monooleatel). TPABr was the smallest template among these four and is generally used to make microporous zeolite (*i.e.* ZSM-5). $C_{14}TMABr$ is an ionic surfactant. It is one of the alkylammonium salts, $C_nH_{2n+1}(CH_3)_3\text{-NBr}$ (n = 8, 10, 12, 14, 16, 18), serving as templates for making mesoporous silica (Huo et al., 1996). $EO_{20}PO_{70}EO_{20}$ is a tri-block-copolymer. Tween 80 is a non-ionic surfactant, which is a mem-

[1] 丁致遠
[2] 吳鎮安
[3] 萬本儒, To whom all correspondence should be addressed
[4] 吳文發

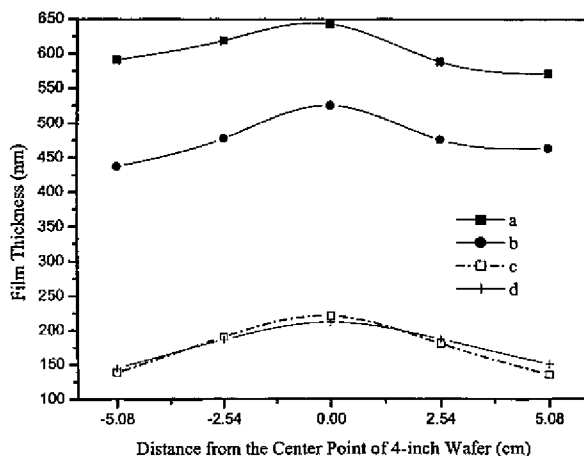


Fig. 1. Effects of spin speeds and TEOS concentration on film thickness. The preparation conditions were: a: TEOS/EtOH = 1/8 (molar ratio), 1700 rpm for 30 s then 2600 rpm for 30 s; b: TEOS/EtOH = 1/8, spin rate 2600 rpm for 30 s; c: TEOS/EtOH = 1/24, 1700 rpm for 30 s; d: TEOS/EtOH = 1/24, 2600 rpm for 30 s.

ber of polyoxyethylene(20) sorbitan compounds. Both $EO_{20}PO_{70}EO_{20}$ and Tween 80 were also used for the synthesis of mesoporous materials in the past (Zhao et al., 1998b). In this research, films from TEOS sol-gel containing these four templates were successfully prepared. The effects of templates on film dielectric constants were measured and compared.

EXPERIMENTAL

Synthesis

Porous silica films were prepared by a spin-on process. The sol-gel deposition solution was from a mixture of TEOS (1 M), deionized water (4~12 M), ethanol (8~24 M), hydrochloric acid (0.24~0.72 M), and templates (the weight ratio of template/TEOS is 0.4 in all experiments). If not specified in this paper, Tween 80 was the template usually used for the preparation of coating solution for examining the coating process. All the chemicals are commercially available from Acros. The coating solution was stirred at room temperature. The resulting solution was spin-coated on a silicon wafer with an SSP-01A spinner (King Polytechnic Engineering CO.). If not specified in this paper, generally the spin speed was maintained at 2600 rpm for 30 s. After spin coating, the film was baked at 106°C for 3 h and calcined at 560°C (the temperature increasing rate was 3°C/min) in the air. The calcination process was performed with a type 48000 furnace (Barnstead | Thermolyne). At last, to make the film hydrophobic, the film was immersed in a silane solution to graft silane group onto the surface. Usually 150~200 g silane solution was used for grafting.

Characterization

The film thickness was measured by an ellipsometer (n & k analyzer). For capacitance measurement, array of aluminum dots with area of 0.0052 cm^2 and thickness of 500 nm (approximately) were formed by the condensation of aluminum vapor through an aluminum shield mask. Capacitance measurements were performed with a Keithley package 82 system. The frequency and the oscillation level were 1 M Hz and 100 mV, respectively. The dielectric constant was calculated from the capacitance, the film thickness and the area of the electrode. The FTIR spectra were measured with a Bomem MB 100.

RESULTS AND DISCUSSION

Film thickness control

The first three stages of film preparation are: coating solution preparation, spin coating and heat treatment. During the preparation of the coating solution, TEOS reacts with water and is hydrolyzed to form Si-OH groups. Since Si-OH can interact with the hydrophilic segments of the organic template, it coagulates around the template and then is polycondensed with another Si-OH group to form a Si-O-Si structure. During these reactions, hydrochloric acid acts as a catalyst. Therefore, the concentrations of TEOS, water and hydrochloric acid should influence the hydrolysis and the condensation rates of TEOS, and also influence the silica concentration in the sol-gel solution. During the spin coating of sol-gel solution on a silicon wafer, the solution is spun off and the evaporation of ethanol transforms the liquid film on the silicon wafer into a solid state. Later, the film is baked to repel the residual solvent and to enhance the interaction between the film surface and the silicon surface. Finally, the calcination process is used to burn off the organic template from the film and to make the film porous. In the porous film preparation process described above, several factors influencing the film thickness can be proposed. First, different TEOS molar ratios in the solution should result in different silica concentrations in the sol-gel, which may cause different film thickness after the spin coating process. Second, different spin speeds may affect both the evaporation of the solvent and the amount of solution adhered to the wafer. Third, different temperature programs for the calcination step may cause the film to shrink to different extents and,

C.E.P.S.

hence, influence the film thickness. Therefore, in order to know which factor influences the film thickness the most, the effects of the TEOS concentration in the solution, the spin speed and the calcination process on the film thickness were investigated in this research.

Figure 1 shows the effects of spin speeds and TEOS concentrations on the film thickness. It can be observed that no matter what the spin speed or TEOS concentration were, all of the films possessed the highest film thickness in the center part of the wafer, and the thickness gradually decreased when the radius was increased. This is because the spin rate increases along with the increase of the centrifugal force and shear force, when the radius is increased; therefore, it causes more solution to spin out from the wafer. Figure 1 also shows that the films prepared from the coating solutions with concentrated TEOS (a, b in Fig.1) were far thicker than the others. Since TEOS acts as the silica source, the solution with more concentrated TEOS is expected to possess more silica and consequently higher viscosity. Therefore, it is more difficult to be spun off during the spin coating process. In addition, for a more concentrated solution, more solids are left after the solvent evaporates. Thus, the thicker film obtained by the more concentrated solution is contributed by both flow and evaporation effects. Similar relationships between the film thickness and the concentration were also found and reported in the research work by Meyerhofer (1978) and Sukanek (1985). Furthermore, in Fig. 1, it can be observed that the film thickness was changed with the spin speed, when the same TEOS concentration was used for the preparation of film. It is found in Fig.1 when the same coating solution with the ratio of TEOS/EtOH = 1/8 was used, the film thickness from spin speed 1700 rpm for the first 30 s and 2600 rpm for the later 30 s was much higher than that from 2600 rpm only for 30 s. This suggests that the film had become immobile in the first 30 s. The thinning of the film in the later time period is mainly resulted from the evaporation of the solvent. In other words, the spin speed in the first 30 s spinning time is more important than those in the later time period. However, the influence of the film thickness from spin speed is less pronounced for the coating solution with less TEOS, *i.e.*, TEOS/EtOH = 1/24 in Fig.1. This is because the films were thinner than those from TEOS/EtOH = 1/8. The effect from the interaction between the coating solution and the silicon wafer at the interface was stronger, which resulted in a smaller effect from the spin speed.

Figure 2 shows the effects on film thickness from the calcination processes. It is found that films were thinner after a faster calcination process. Therefore, it can be observed that the film from 3°C/min

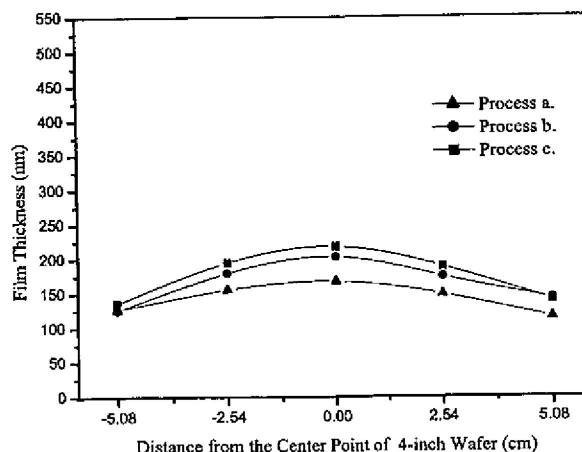


Fig. 2. Effects of calcination programs on film thickness. The molar ratio of components in the coating solution is TEOS/EtOH/H_2O/HCl = 1/24/12/0.72. Process a: films were heated to 560°C at the rate of 3°C/min and maintained at 560°C for 0.5 h; b: films were heated to 400°C at 1°C/min and maintained at 400°C for 0.5 h; c: films were heated to 150°C at 1°C/min, maintained at 150°C for 0.5 h; then heated to 300°C at 1°C/min, maintained at 300°C for 0.5 h; finally, films were heated to 400°C at 1°C/min, maintained at 300°C for 0.5 h.

temperature increasing rate to 560°C (process a) is the thinnest one. And the film from 1°C/min temperature increasing rate to 400°C (process b) is thinner than that from 1°C/min process in which the temperatures were stopped at 150 and 300°C for 0.5 h respectively (process c). It is apparent that stopping the temperature increase at 150 and 300°C slowed down the calcination process, and transferred more heat generated from burning template in the film to the surrounding, which results in a lower temperature in the film. These indicate that there is significant heat transfer resistance within the film during calcination. Therefore, the temperature of the film in process a, shown in Fig. 2, should be the highest, and the temperature of the film in process b should be higher than that in process c. Higher temperatures should cause more film shrinkage. This is because besides the burning away templates, the condensation of Si-OH sites in the film also takes place. A higher temperature in the film causes more condensation to occur. Hence, it is reasonable that a thinner film would be produced by a faster calcination process.

Although the spin speed and the calcination process did affect the film thickness, their impacts were weak. From the results in Figs.1 and 2, it is clear that the concentration of TEOS in the sol-gel solution influences the film thickness the most.

C.E.P.S.

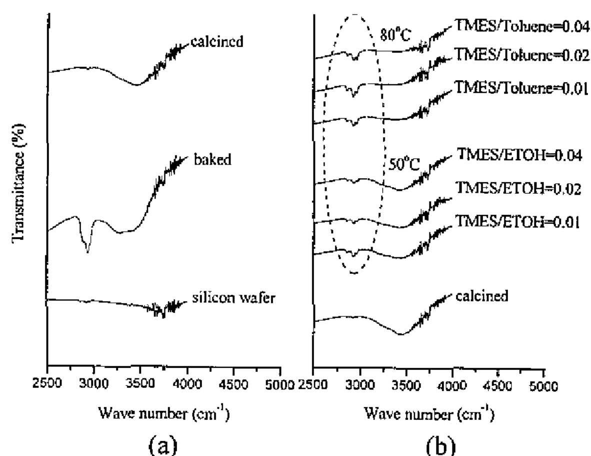


Fig. 3. FTIR spectra of the films modified at different temperatures. (a) Spectra of silicon wafer, baked film and calcined film; (b) spectra of films modified under different conditions. The molar ratio of components in the coating solution is TEOS/EtOH/H_2O/HCl = 1/8/4/0.24.

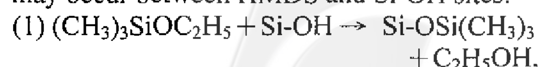
Surface modification

After calcination, the organic templates in the film are removed and some Si-OH sites are still left on the pore surface. Si-OH possesses hydrophilic property and can adsorb moisture from the air. Because the dielectric constant of water is 78, the adsorption of water on the surface will lead to an elevation of the dielectric constant of the porous silica film on the silicon wafer. Therefore, surface modification to eliminate Si-OH and transform Si-OH to a hydrophobic unit is important for producing low k materials from the templating process.

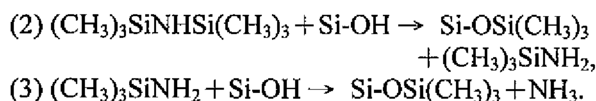
The surface modification method used in this research was to graft silane compounds (e.g. TMES (trimethylethoxysilane) or HMDS) onto the film. By removing H atom and grafting silanes on Si-O of Si-OH, the surface becomes hydrophobic. The grafting process developed in this research was to immerse the film in a silane solution at a certain temperature. After grafting, the film was washed by a solvent, and dried in the air. Therefore, the first issue in this research on the surface modification process was to determine the grafting temperature. To save energy and improve safety, low temperatures were preferred, as a result, 50°C and 80°C were tested. Either ethanol or toluene was used as the solvent, depending on the surface modification temperature. Moreover, in order to check whether the grafting process was complete, FTIR was applied to characterize the surface. Some typical FTIR results are shown in Fig.3. It can be observed in Fig. 3(a) that before spin coating, only very trace absorption bands around wave number 2900 cm^{-1}, which corresponds to C-H bonding, can be found on the silicon wafer. These trace signals were due to the contamination. However, after the film was spin-coated on the silicon wafer and baked at 106°C, strong absorption bands around 2900 cm^{-1} appeared. This indicates that a large amount of organic template existed in the film. Moreover, in Fig. 3(a), absorption bands around 3500 cm^{-1} (wave number from 3000 to 3800 cm^{-1}) can also be observed. These bands corresponded to those from O-H bonding, which resulted from the adsorbed water and from Si-OH sites in the film. Nevertheless, after calcination, the bands from O-H bonding became weaker but still remained strong, and those from C-H bonding disappeared. The disappearance of C-H bonding indicates that the calcination process can be an effective way to burn off organic templates in the film. Moreover, the decrease of the O-H band intensity should be due to the condensation reaction of Si-OH sites in the film. However, the condensation reaction was apparently not complete, the strong band intensity from O-H suggests a significant number of Si-OH sites for the adsorption of moisture still remain in the film after calcination. Therefore, it is necessary to develop a surface modification process to remove these O-H sites in order to reduce the dielectric constant of the film.

FTIR spectra of films modified with TMES in different solutions at 50°C and 80°C were shown in Fig. 3(b). The films were calcined prior to the surface modification. Since there were no organic compounds in the films after calcination, the bands corresponding to C-H bonding marked in Fig. 3(b) were the evidence from grafted silane molecules in the films. It is clear from these results that silane molecules were successfully grafted onto the film surface, no matter what silane concentration or modification temperature was used. Moreover, it can be observed that the band intensity corresponding to O-H bonding of Si-OH was more attenuate when the temperature for surface modification was at 80°C. It suggests that the grafting process was more successful at 80°C. Therefore, in the later experiments, all the modification process were conducted at 80°C.

To further investigate the surface modification process, measurements of dielectric constants of the surface modified films were used as a basis for comparing the completeness of surface modification in the later research. Because the dielectric constant is quite sensitive to both Si-OH sites and adsorbed water in the film, it is a direct way for the detection of the effectiveness of surface modification. The silanes used in this study were TMES and HMDS. Their surface modification reactions are illustrated as follows: reaction (1) denotes the grafting of TMES onto Si-OH in the film; reaction (2) and (3) are the reactions may occur between HMDS and Si-OH sites:



(1) $(CH_3)_3SiOC_2H_5 + Si\text{-}OH \rightarrow Si\text{-}OSi(CH_3)_3 + C_2H_5OH$,



(2) $(CH_3)_3SiNHSi(CH_3)_3 + Si\text{-}OH \rightarrow Si\text{-}OSi(CH_3)_3 + (CH_3)_3SiNH_2$,

(3) $(CH_3)_3SiNH_2 + Si\text{-}OH \rightarrow Si\text{-}OSi(CH_3)_3 + NH_3$.

Table 1 shows the dielectric constant of the film modified by these two different silanes. A modification process that produces films with lower dielectric constant should be more effective. It can be observed that at the same molar ratio of silane to toluene, the films modified by HMDS always possessed lower dielectric constants than those by TMES. Therefore, it can be concluded from these experiments that HMDS was more effective for modifying the film. There may be two reasons for this outcome. First, a HMDS molecule has two groups of silane, as shown in reaction (2), thus, it has more effective silanes for the surface modification compared to TMES. Second, a HMDS molecule would produce a smaller silane molecule after it reacts with a Si-OH, as shown in reaction (2). This silane is even smaller than a TMES molecule. It should be able to penetrate deeper in the micro-pores formed in the film. Therefore, the surface modification was more complete by using HMDS than by TMES.

The effects of HMDS/toluene ratios on the surface modification of the films are shown in Table 2. It can be observed that the dielectric constant decreased from 3.6 to 2.4 when the molar ratios of HMDS to toluene increased from 0.04 to 1. This indicates that more Si-OH on the film surface can be grafted with silane when the concentration of HMDS in the solution increased. However, when the molar ratio of HMDS/toluene was higher than 1, the dielectric constants of the films started to increase slightly, and then essentially remained the same until pure HMDS solution was used for the surface modification. This may suggest that every possible grafted Si-OH site on the pore surface of the film had been grafted with silane groups, when the ratio of HMDS/toluene was 1. Therefore, the increase of the ratio of HMDS/toluene to more than 1 had no means for reducing Si-OH sites on the film; on the contrary, it may cause more amount of HMDS physically adsorbed on the surface of the film. These physically adsorbed HMDS can react with moisture to form Si-OH. The slight increase of dielectric constant might be simply from these unexpected trace amount of Si-OH groups contaminated on the surface of the film.

Table 1. Dielectric constants of the films modified by different silane and different solution concentrations. The molar ratio in the coating solution is $TEOS/EtOH/H_2O/HCl$ = 1/8/4/0.24.

Silane	Silane/Toluene (molar ratio)	Dielectric Constant
TMES	0.04	6.8
	0.2	5.5
HMDS	0.04	3.6
	0.2	3.3

Table 2. Dielectric constants of the films modified by solution with different HMDS solution concentrations. The molar ratio in the coating solution is $TEOS/EtOH/H_2O/HCl$ = 1/8/4/0.24.

HMDS/Toluene(molar ratio)	Dielectric Constant
0.04	3.6
0.2	3.3
1	2.4
5	2.7
Pure HMDS (150g)	2.7

Effects from different templates

In this research, TPABr, $C_{14}TMABr$, $EO_{20}PO_{70}EO_{20}$ and Tween 80 were examined as templates in TEOS solution for producing porous silica films. $C_{14}TMABr$ is an ionic surfactant. Tween 80 is a non-ionic surfactant. The molecular structures of these four templates are shown in Fig. 4. The hydrophobic segment of each molecule is circled in the figure. It can be observed that both TPABr and $C_{14}TMABr$ are ammonium bromide compounds. The only difference between these two is the size of hydrophobic groups, in which the one in TPABr is much shorter than that in $C_{14}TMABr$. Therefore, even if there are micelles formed in a polar solution (*i.e.*, ethanol in this research), those from TPABr should be much smaller than those from $C_{14}TMABr$. However, the sizes of hydrophobic groups in $C_{14}TMABr$ and in Tween 80 are similar, and there is a distinct difference between the segments of hydrophobic and hydrophilic groups in $C_{14}TMABr$ and also in Tween 80. The sizes of micelles formed from these two surfactants should be similar. Nevertheless, it is noticed that there is little difference between the segments of hydrophobic and hydrophilic groups in $EO_{20}PO_{70}EO_{20}$. In addition, the molecular size of this copolymer is much larger than those of the others used in this research. Therefore, large micelles may not be easily formed from $EO_{20}PO_{70}EO_{20}$. It is more likely that this copolymer only coagulates, and then acts as an organic template in the solution.

In order to compare the effects of these four templates, all the solution preparation conditions were kept the same (including the weight ratio of template to TEOS). It can be found in Table 3 that the dielectric constant of the film was much higher when TPABr was used as a template. It is even higher than that of a dense SiO_2 film reported in the literature (Martin et al., 2000). There may be two reasons for this outcome. First, it is difficult for TPABr molecules to form micelles in the coating solution. Hence, no significant amount of pore volume

C.E.P.S.

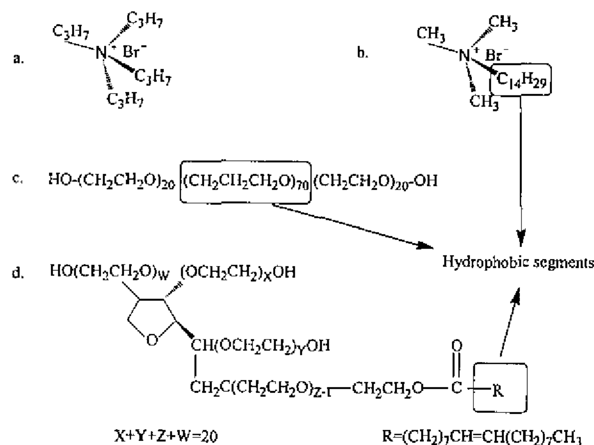


Fig. 4. Structures of the templates used in this research. a: TPABr; b: C_{14}TMABr; c:$EO_{20}PO_{70}EO_{20}$; d: Tween 80.

Table 3. Dielectric constants of films with different templates. The molar ratio in the coating solution is TEOS/EtOH/H_2O/HCl = 1/8/4/0.24. The surface modification process was performed in a HMDS/toluene solution with a molar ratio of HMDS/toluene = 1.

Template	Dielectric Constant
TPABr	8.8
C_{14}TMABr	2.8
$EO_{20}PO_{70}EO_{20}$	2.5
Tween 80	2.4

existed after film calcination. Second, only micro-pores instead of meso-pores were formed in the film, and the bigger silane molecules were not able to diffuse into the pores for modifying the surface. Consequently, the surface modification process was not complete and a significant amount water adsorbed in the film caused the high dielectric constant.

For the films prepared from the solutions with C_{14}TMABr, $EO_{20}PO_{70}EO_{20}$ and Tween 80 as templates, it can be found in Table 3 that the dielectric constants of these films were below 3. This means that these three compounds can be good candidates as organic templates in the colloid solution for the preparation of porous silica films with low k property. For C_{14}TMABr and Tween 80, this is due to micelles formed in the coating solution. Because the size of these micelles is much larger than that of a single molecule, even the space occupied by these micelles in the film experiences contraction during the calcination process, the meso-pores should remain in the film. Therefore, these pores can allow silane molecules to diffuse in and react with silanol groups on the pore surface. And the surface modification process was more complete for the films prepared with these surfactant templates. Nevertheless, it is noteworthy that although there are no distinct hydrophobic and hydrophilic segments in $EO_{20}PO_{70}EO_{20}$, and the micelles may not be possibly formed from this copolymer, the low k value of the film made with this template was almost as small as that from Tween 80, as shown in Table 3. This suggests that the pore volume in the film should be close to that made with Tween 80. Therefore, it can be concluded from this research that the formation of micelles is not the only way, the coagulation of a dissolved polymer molecule in the solution may be another way for making an appropriate template for porous silica films.

Although low dielectric constant films can be prepared by using C_{14}TMABr as a template, the bromine ion in C_{14}TMABr is a hidden problem. The charged bromine ions in C_{14}TMABr may remain in the film, which may result in a higher k value for the film. Therefore, it can be observed in Table 3 that the k value of the film with C_{14}TMABr as the template is higher than those from Tween 80 and $EO_{20}PO_{70}EO_{20}$. Moreover, for the application in intermetal dielectric, a film with a lot of charged ions is not preferred. Thus, it could be inferred that the alkylammonium salt may not be a suitable template for the preparation of low k porous silica films in the future.

$EO_{20}PO_{70}EO_{20}$ and Tween 80 do not have charged ions. Therefore, the porous films prepared from them would not be suffered from charged ions. From Table 3, the film using Tween 80 as a template exhibits the lowest dielectric constant and is potentially useful in the preparation of low k films in the future. It should be noted that the superior property of Tween 80 for preparing low k films is reported for the first time.

CONCLUSION

Factors influencing the film thickness are the TEOS concentration of coating solution, the spin and the calcination processes. It was found in this research that the concentration of TEOS in the solution affects the film thickness the most. In the surface modification process, the effects of the reaction temperature, the type of silane (*i.e.* TMES or HMDS) and the silane concentration were investigated. It was found that the surface modification was more complete when the temperature was 80°C and when HMDS was used as the silane agent. Moreover, films prepared with different templates (TPABr, C_{14}TMABr, $EO_{20}PO_{70}EO_{20}$ and Tween 80) were compared. The films using $EO_{20}PO_{70}EO_{20}$ and Tween 80 as templates possessed lower dielectric constants, and showed great potential in intermetal dielectric applications. Moreover, the film with Tween 80 (polyoxyethylene (20) sorbitan) possessed the lowest dielectric constant (k = 2.4), which made this compound to be one of the promising templating

C.E.P.S.

agents to make low k porous silica films in the future.

ACKNOWLEDGEMENT

The spin coating process and some of the ellipsometer measurement were carried out in the laboratory of Professor Wen-Chang Chen. FTIR measurements were carried out in the laboratory of Professor Soofin Cheng. Both professors are serving in National Taiwan University. The authors wish to thank them for their help and consulting. The financial support from China Petroleum Company is also appreciated.

NOMENCLATURE

k dielectric constant of a material

REFERENCES

Baskaran, S., J. Liu, K. Domansky and N. Kohler, "Low Dielectric Constant Mesoporous Silica Films through Molecularly Templated Synthesis," *Adv. Mater.*, **12**, 291 (2000).

Honma, I., H. S. Zhou, D. Kundu and A. Endo, "Structural Control of Surfactant-Templated Hexagonal, Cubic and Lamellar Mesoporous Silicate Thin Films Prepared by Spin-Casting," *Adv. Mater.*, **12**, 1529 (2000).

Huo, Q., D. I. Margolese and G. D. Stucky, "Surfactant Control of Phases in the Synthesis of Mesoporous Silica-Based Materials," *Chem. Mater.*, **8**, 1147 (1996).

Jo, M. H., H. H. Park, D. J. Kim, S. H. Hyun, S. Y. Choi and J. T. Paik, "SiO_2 Aerogel Film as a Novel Intermetal Dielectric," *J. Appl. Phys.*, **82**(3), 1299 (1997).

Martin, S. J., J. P. Godschalx, M. E. Mills, E. O. Shaffer II and P. H. Townsend, "Development of a Low-Dielectric-Constant Polymer for the Fabrication of Integrated Circuit Interconnect," *Adv. Mater.*, **23**, 1769 (2000).

Meyerhofer, D., "Characteristics of Resist Films Produced by Spinning," *J. Appl. Phys.*, **49**, 3993 (1978).

Ramos, T., K. Roderick, A. Maskara and D. M. Smith, "Nanoporous Silica for Low K Dielectrics," *Mat. Res. Soc. Symp. Proc.*, **443**, 91 (1997).

Sukanek, P. C., "Spin Coating," *J. Imag. Technol.*, **11**(4), 184 (1985).

Yang, H., A. Kuperman, N. Coombs and G. A. Ozin, "Free-Standing and Oriented Mesoporous Silica Films Grown at the Air-Water Interface," *Nature*, **381**, 579 (1996).

Zhao, D., P. Yang, N. Melosh, J. Feng, B. F. Chmelka and G. D. Stucky, "Continuous Mesoporous Silica Films with Highly Ordered Large Pore Structures," *Adv. Mater.*, **10**, 1380 (1998a).

Zhao, D., Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, "Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures," *J. Am. Chem. Soc.*, **120**, 6024 (1998b).

(Manuscript Received May 24, 2002)

以模版法製備低介電二氧化矽薄膜的研究

丁致遠　吳鎭安　萬本儒
國立台灣大學化學工程學系

吳文發
國家奈米元件實驗室

摘　要

本文探討以有機物爲模版，開發孔洞型二氧化矽低介電薄膜的製備程序，研究中使用了幾種可溶於矽膠體溶液之有機物(包含離子型及非離子型界面活性劑)爲模版。二氧化矽薄膜孔洞的形成，是藉由鍛燒程序中，這些有機物的燒除而形成。本研究並探討製備程序中膜厚的控制及薄膜表面改質的方法。由研究結果發現，膜厚可由溶液組成，旋轉塗佈轉速及鍛燒升溫速度加以控制，但是影響膜厚的主要因素是塗佈溶液中二氧化矽前驅物 TEOS(tetraethyl orthosilicate)的濃度，而旋轉塗佈轉速及鍛燒升溫速率則僅會稍許改變膜厚。另外，表面改質的目的是爲使薄膜表面產生疏水性，本研究已探討了反應溫度、矽烷種類(改質劑)及濃度的效應，由研究得知以甲苯(toluene)溶液中的 HMDS(1,1,1,3,3,3-hexamethyl disilazane)在 80℃ 下對表面改質效果最佳。本研究同時也嘗試四個不同種類的模版試劑，結果發現以 Tween 80(polyoxyethylene(20) sorbitan monooleatel)非離子型界面活性劑所得的薄膜介電值最低，因此在未來孔洞型二氧化矽低介電薄膜的製備上，該模版之應用應深具潛力。