Electrical Instabilities of Mesoporous Silica Thin Films

Mai Xuan Dung and Hyun-Dam Jeong[†]

Abstract

On the surface of mesoporous silica thin films (MSTF) which were fabricated by sol-gel approach there are existences of water and three different silanol types including chained, germinal and isolated silanol. Their amounts changes as a function of aging time of used sol solution, as confirmed by FT-IR. The adsorbed water generates ionic carriers such as H+ and OH- and passivates the Si dangling bonds at the interface of silicon wafer-MSTF. The ionic carriers can not only transport across the thickness of thin film to enhance the leakage current but also diffuse toward the silicon wafer-MSTF interface to depassivate Si dangling bonds. On the other hand, chained silanols or germinal silanols promote the moisture adsorption of MSTF and tend to form strongly hydrogen bonded systems with adsorbed water molecules resulting in very high dielectric constant. Isolated silanol, on the contrary, affects less on electrical properties of thin film.

Key words : Mesoporous Silica Thin Films (MSTF), Silanol, FT-IR

1. Introduction

Mesoporous silicate materials have been applied widely as catalysis, separation and sensors. Because of its high porosity, mesoporous silica thin film (MSTF) is believed to be a promising candidate for the next ultralow-k dielectric thin films for integrated circuit applications[1]. Ordinarily, the porosity of porous material accounts directly for its refractive index or the electronic polarization term of its dielectric constant (k). The two other parts of k are ionic and orientational polarizations which are related to the fluctuation of electrons in chemical bonds and orientational response of permanent dipole moments existing within porous layer, respectively. However, as a porous silicate, MSTF easily adsorbs moisture which not only enhances the formation of dipolar groups such as silanols or hydrogen bonded silanol-water systems to increase dielectric constant but also accelerates the leakage current regardless to its structural propertie[2-6]. Especially, MSTF that are obtained from solution processes usually has higher dielectric constant value, compared to that (c.a. 4.0) of tra-

ditional SiO_2 thin films fabricated by conventional chemical vapor deposition. Water is though to be the originally harmful factor degrading MSTF. Once water is adsorbed, it can reacts with -Si-O-Si- bonds within MSTF to form additional silanol (-Si-OH) groups. Furthermore, Uchida et al showed that the total amount of silanol on the surface of MSTF is proportional to its dielectric constant[3]. Unfortunately, the distinctive effect of different silanol types were not mentioned yet. On the other hand, Ramanath and groups pointed out that the excess adsorbed water within mesoporous silicate passivates Si dangling bonds at the interface between silicon wafer and silicate layer causing the appearance of deep depletion region in Capacitance-Voltage curve[4]. When the silicate layer is cured in nitrogen environment at high temperatures, the remaining adsorbed water also generates ionic carriers by react with surface silanol groups or Si-O-Si bonds until it is completely evaporated out. In our opinion, the effects of silanol types on the electrical properties of mesoporous silicate are different because of their reactivities with water. Chained silanol groups form hydrogen bonds more energetically with water that germinal silanol or isolated silanol groups do. Understanding the formation of ionic carriers such as OH- or H+ and their transportation in mesoporous silicate when it is cured in ambient conditions could give us useful evident for direct applications such as humidity sensor, catalyst or considering further treat-

Department of Chemistry and Institute of Basic Science, Chonnam National University, 300, Yongbong-dong, Buk-gu, Gwangju, 500-757, Republic of Korea

[†]Corresponding author: hdjeong@chonnam.ac.kr

ments needed for electronic applications.

Up to date, changing silica resources or modification MSTF surface with organosilane compounds have been done to increase the hydrophobicity of MSTF, prevent it from moisture attack[7-9]. However, the mechanism in which the electrical properties of MSTF are affected by the interaction between moisture and silanol groups has not yet discussed in detail.

In this article, we discuss the effects of different silanol types on the electrical instabilities of mesoporous silica thin film and also classify their affinities to the moisture adsorption.

2. Experimental Section

MSTFs were synthesized by convenient Evaporation - Induced Self - Assembly (EISA) route, adapted from reference 10. A homogeneous acidic solution with molar ratio: 1 Tetraethoxylsilicate (TEOS): 34 Ethanol (EtOH): 5 water (H2O): 0.004 hydrochloric acid (HCl): 0.21 cetyltrimethylamonium bromide (CTAB) was stirred at the speed of 500 rpm at 65ºC in a 40ml vial. Original HCl (35%) was purchased from DC Chemical Co.Ltd (Korea). Double distillated water was used. The other chemicals were purchased from Aldrich. Aliquots of the sol solutions were taken at various aging times (1, 2, 3.5, 5, 10 and 20 hours) and coated on silicon wafers in ambient conditions by spin -coater (SPIN 1200, Midas System, Korea) at 2500 rpm for 25 seconds. Low resistivity (<0.005 Ωcm) silicon wafers as well as high resistivity (1-30 Ωcm) silicon wafers (Silicon Materials Inc) were used for different measurement purposes. Thin films were then placed on a hot plate at 80ºC for over night. Finally, the organic surfactant was removed by calcination at 450ºC (3o/min) for 4 hours. The samples were kept in vacuum till for further use. In this article, sample 1h means that it was made from 1hour aged sol solution and so on. Metal-insulator-semiconductor (MIS) and metal-insulator-metal (MIM) devices were fabricated similarly to reference[13]. Capacitance - voltage (C-V) and current - voltage (I - V) measurements were carried out at various temperatures by HP4284LCR meter under ambient atmosphere. The dielectric constants of MSTFs were calculated by the following equation:

$$\varepsilon = \frac{C_{max}A}{\varepsilon_o d}$$

eq. (1)

Whereby, ε and εo (ε0=8.854.10-14 F/cm) are the dielectric constants of MSTF and vacuum, respectively. Cmax is the maximum value of the capacity C. A is the area of the aluminum electrode, calculated from microscope image (Olympus SZ61) and d is the thickness of MSTF obtained from FE-SEM image (JSM-7500F +EDSO Oxford). FTIR spectra were performed on high resistivity Si wafer samples by Bruker FS66v/S spectrometer at a resolution of 2 cm^{-1}. All of the samples were exposed to air at room temperature overnight before measurements. The results were obtained after scanning 192 times and the signal recorded on a high resistivity silicon wafer was used for background correlation.

3. Result and Discussion

Chemical surface of MSTF were characterized by FT-IR and the spectra are shown in Fig. 1(a) including several characteristic regions. The high frequency region from 2800 to 4000 cm^{-1} show various O-H vibration modes:11 such as isolated silanol ~3740cm^{-1}, hydrogen-bonded (H-bonded) OH group of geminate silanols ~3600-3700 cm^{-1}, H-bonded OH group silanols in chain ~3200-3650 cm^{-1} and OH group of adsorbed water ~3300-3500 cm^{-1}. Also the peak of OH group of adsorbed water can be cross checked from the peak ~1630 cm^{-1} due to scissor bending vibration of water molecule. In fact, the areas of ~1630cm^{-1} band were calculated for comparison the relative amounts of adsorbed water on different MSTFs, Fig. 1(c). As the aging time increases the amount of adsorbed water and the nature of silanol on the surface of MSTF were changed. From three samples 5 h, 10 h and 20 h, it is evident that the intensity of chained silanol is decreasing and at the same time that of isolated silanol is increasing. Regardless to the change in the structure of MSTF, the differences in surface properties including adsorbed water and silanol nature are going to be discussed based on dielectric constant, leakage current and C-V characteristics.

With an assumption that physical adsorbed water is evaporated completely from the MSTFs above its boiling point (100ºC).13 We figured out the values of as a function of the inverse Kelvin temperature (1/T) from the four experimental points above 100ºC. They were linear graphs because in the Debye equation (eq.2)
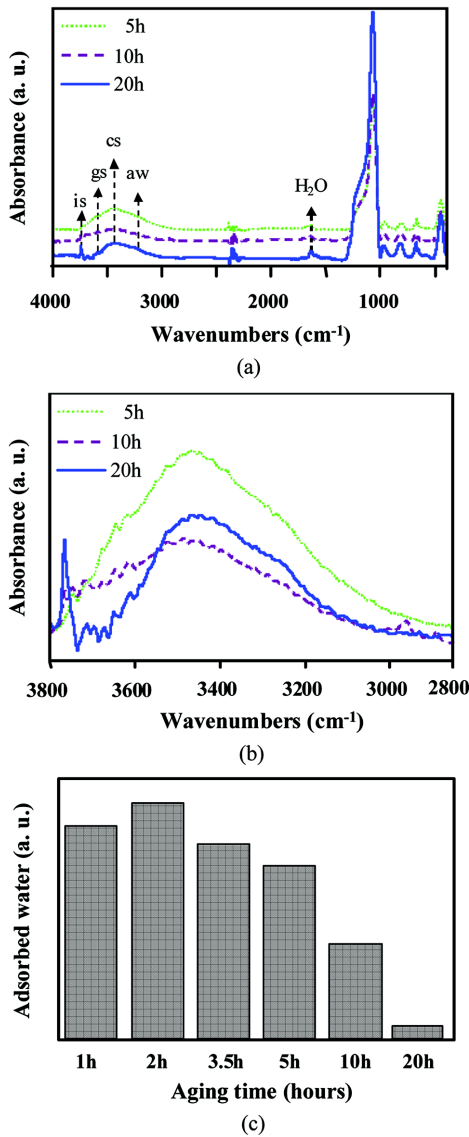
(a)

(b)

(c)

Fig. 1. FT-IR characterizations of mesoporous thin films. (a): Surface components of MSTF; (b): the high frequency region and (c): the relative amounts of adsorbed water calculated from the areas of the ~1650 cm^{-1} bands of different samples which were obtained from sol solutions with aging time ranging from 1 hour to 20 hours. (aw), (cs), (gs) and (is) are adsorbed water, chained silanol, geminate silanol, and isolated silanol, respectively.

$$\frac{\varepsilon-1}{\varepsilon+2} = \sum \frac{N_i}{3\varepsilon_o}\left(\alpha_i + \frac{\mu_i^2}{3kT}\right) \qquad \text{eq. (2)}$$

Ni (density), ai (polarizability), μi (dipole moment) of the ith component and k (Boltzmann constant) are con-
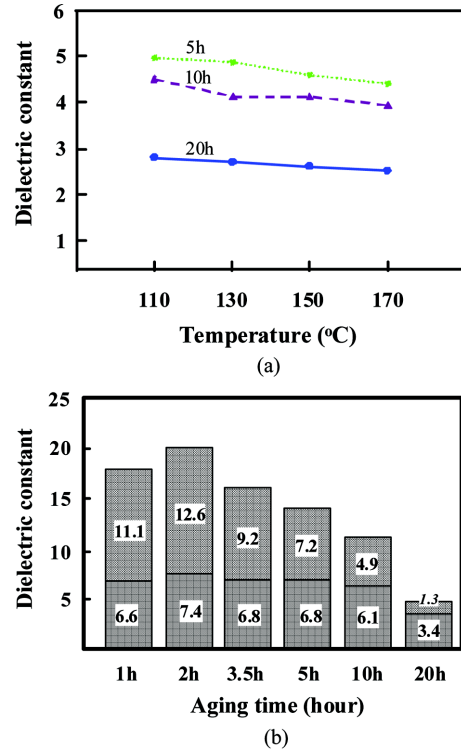

(a)

(b)

Fig. 2. The changes in total dielectric constant of mesoporous thin film as function of temperature (a) and aging time of sol solution (b). In (b), the lower parts are the attributions of physical adsorbed water component to total dielectric constants and the upper parts are the sums of attributions of strongly adsorbed water, silanol groups and silicon oxide to the total dielectric constants of MSTFs at room temperature.

stants. The dielectric constants of MSTF without physical adsorbed water was then calculated by extrapolation the above function to room temperature T=298K. The contribution of adsorbed water component to the dielectric constant of MSTF at room temperature was the difference between the experimental value and the extrapolated value. These values are demonstrated as in the Fig. 2(b).

They are fairly proportional to the amounts of physical adsorbed water, Fig. 1 (b), in agreement with Debye equation, (eq. 2). However, the remaining parts of dielectric constants, shown as the upper parts in Fig. 2(b), are several times greater than that of dense SiO$_2$ (~4.0) except for the sample 20 h. This is attributed by the remaining components such as strongly adsorbed water and silanol groups which could form highly polar dipole

moments under applied bias voltages.

To clarify the effects of these components on the dielectric constant, leakage current and device instabilities three samples 5 h, 10 h and 20 h are chosen for further investigation because of their distinguishable surface properties. In the high frequency region, Fig. 1(a) shows the change in the intensities of three types of silanol groups: chained silanols, geminate silanols and isolated silanols as the function of aging time. As the aging time increases from 5 hours to 20 hours, the intensity of geminate silanol which is not overlapped by the adsorbed water decreases and that of isolated silanol increases simultaneously. Unfortunately, this trend is not supported by the change in the intensity of chained silanol band which is overlapped by adsorbed water. From the concepts of hydrolysis-condensation reaction, that the formation of isolated silanol groups is due to the decrease in the number of silanol groups in chains as per the following discussion. As aging progresses, small linear silica clusters tend to form bigger cyclic oligomers by cluster aggregation or by fractal growth mechanisms through condensation reaction[15]. After coating, preformed silica oligomers condensate together to build up silica skeleton through their edges connection. As the result, the nature of silanol on the MSTF is strongly dependent on the size and shape of silica oligomers in the initial sol solutions regardless to further heat treatments. Within our experimental conditions, the decrease in the intensity of geminate silanol accompanied by the increase of isolated silanols when the sol solutions were aged gradually to 20 hours is attributed to the formation of large cyclic silica oligomers. In the case of sample 20 h, the intensity of isolated silanol band is very high, where as the intensity of germinated silanol is very low which indicates that silanol groups are almost isolated, Fig 1(inserted a). On the contrary, in sample 5 h, the silanol groups are mostly in chains because of the very high intensities of chained or germinal silanol. The result for sample 10h shows that it has less chained silanols compared to sample 5 h and less isolated silanol compared to sample 20 h. These differences led to the different behaviors of dielectric constant above 100°C as mentioned earlier. While the dielectric constant of the sample 20 h reaches ultralow values (<2.5), the dielectric constant of samples 5 h and 10h are still much higher than that of SiO_2, Fig. 2(a). From the Debye equation, (eq. 2) there are some components that

account for the dielectric constant of MSTF at temperatures above 100°C. They are silanol groups, strongly adsorbed water molecules, silicon oxide skeleton and air. There have been several theoretical models that explain well the effect of the two later components, so called porous structure, on dielectric constant of MSTF such as: parallel capacitor model, serial capacitor model, Lorentz - Lorenz, Maxwell - Garnett, Bruggeman expressions or Rayleigh's method[5,6]. According to these models, the sum of distributions of silica skeleton and air components to the total dielectric constant are much smaller then dielectric constant of SiO_2 (~4.0). Therefore, the excess of dielectric constants of MSTFs are attributed to silanol groups and strongly adsorbed water molecules. Among MSTF samples, sample 20 h contains mainly isolated silanols which are though to be hydrophobic. Because it is well known that adsorbed water molecules form H-bond each other more energetically than they do with isolated silanols. As a result, adsorbed water molecules tend to form clusters which are physically adsorbed and easily evaporated out of silica skeleton, reducing the density of water component. Whereas in sample 5 h and 10 h, silanols are mainly in chains or couples so that they can hold water molecules by forming strong H-bond with them. High water concentrations and silanol densities remaining above 100°C in these samples account for their high values of dielectric constants.

On the other hand, the difference in silanol nature causes two distinguishable shifts in leakage current when MSTFs were annealed at 110°C, Fig. 3. The removal of weakly adsorbed water decreases the leak-
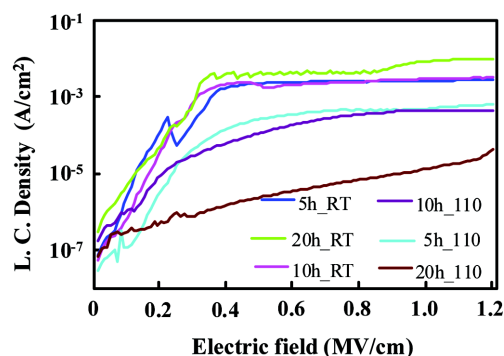

Fig. 3. The change in leakage current across the mesoporous thin film as a function of applied electric field at room temperature and 110°C.

age current 1000 times (shift 2) in case of sample 20 h but nearly 10 times (shift 1) for samples 5 h or 10 h. This difference is due to the concentrations of ionic carriers and their transportabilities formed in MSTFs. In detail, water is easily adsorbed on the surface of MSTFs at room conditions because of capillary force and the adsorption is favored by hydrophilic silanol groups. Adsorbed water molecules are partial dissociated into ionic ions H+ and OH? which could also be formed from the reactions of water and silanol groups or SiO_2. Under external field, these ionic carriers are forced to transport across the MSTFs. These carriers move easily along the H-bonded systems on the inner surface of MSTFs. These systems could be adsorbed water clusters or water-silanol systems. The ready moisture adsorption of MSTFs results in high and similar leakage currents at room temperature. But at the temperatures higher than the boiling point of water (100°C), the physically adsorbed water is mainly evaporated out of MSTFs leaving almost isolated silanols as in case of sample 20 h or H-bonded water-silanol systems as in case of sample 5 h and 10 h. Isolated silanol groups do not support the transportations of ionic carriers because -Si-O-Si- bonds between them act as gaps which restrain the movement of ions resulting in a sharp decrease in leakage current. Otherwise, the remaining H-bonded systems of strongly adsorbed water and chained silanols or at least germinate silanols on the inner surface of samples 5 h and 10 h make their leak-

age currents remaining very high.

The formation of ionic carries in MSTFs is confirmed by capacitance-voltage measurements. As discussed in our last article, the appearance of clockwise hysteresis accommodated with no flat-band voltage (Vfb) indicates the ionic mobile model of C-V curve[12]. Further more, the width of hysteresis loop could be used as an indicator for the concentration of ionic carriers.

As shown in figure 4, when the temperature increases from 110°C to 170°C the widths of hysteresis loops increases gradually in order of: 5 h > 10 h > 20 h. The ionic carriers are formed from the reactions between adsorbed water and silanol groups: [4]

$$Si\text{-}OH + H_2O \text{ (adsorbed)} \leftrightarrow SiO^- + H_3O^+ \quad \text{eq. (3a)}$$
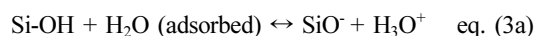
or environmental moisture and Si-O-Si bonds in the silica skeleton:

$$\text{-}Si\text{-}O\text{-}Si\text{-} + H_2O \text{ (Gas)} \rightarrow 2\text{-}SiO^- + 2H^+ \quad \text{eq. (3b)}$$
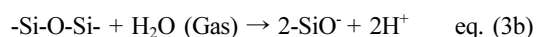
Under our experimental conditions, relative humidity was 60% (measured by Center 310 humidity temperature meter). This wet environment favors the reaction 3b to occur As a result, the concentration of ionic mobiles increases continuously. At room temperature, no hysteresis was observed. This could due to the too low ionic mobile densities which are resulted from water dissociation or it is partially overlapped by the excess moisture. Environmental moisture or adsorbed water also causes another matter of instability of MIS
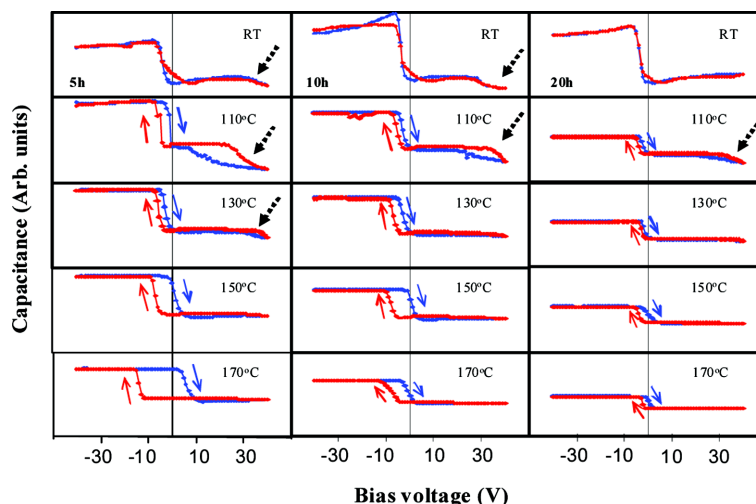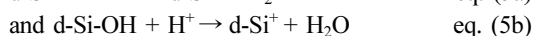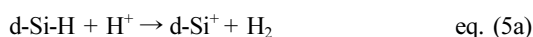

Fig. 4. C-V curves of sample 5 h (left), 10 h (middle), and 20 h (right) at different temperatures. Capacitance was recorded with cyclic -40(V) ~ +40(V) sweep bias voltage.

device which is depletion region in C-V curve when the device is cured in ambient condition. The deep depletion regions appear in all samples in the positive bias voltage direction at room temperature and seem to reach maximum at 110°C and finally disappear at temperatures above 150°C, Fig 4. This phenomenon happens even in water free nitrogen atmosphere.4 The deep depletion region is originated from the passivation of dangling bonds of Si at MSTF - silicon wafer (MSTF-Si) interface caused by excess water:

$$H_2O + 2d\text{-}Si \rightarrow d\text{-}Si\text{-}H + d\text{-}Si\text{-}OH \qquad \text{eq. (4)}$$
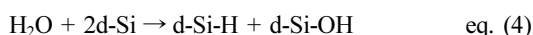
Where d-Si represents a Si dangling bond. This process can take place rapidly even at room temperature due to the low kinetic barrier (≤ 0.04eV). The disappearance of depletion region is resulted from the increase of a reverse process, named depassivation:

$$d\text{-}Si\text{-}H + H^+ \rightarrow d\text{-}Si^+ + H_2 \qquad \text{eq. (5a)}$$
$$\text{and } d\text{-}Si\text{-}OH + H^+ \rightarrow d\text{-}Si^+ + H_2O \qquad \text{eq. (5b)}$$

The ionic carriers that take part in depassivation process (eq. 5a, b) are preformed by reactions (eq. 3a, b) and migrate to MSTF-Si interface by bulk diffusion or surface transport as discussed above. Depassivation (eq.5a, b) is the rate-determining step of the deleting deep depletion region process because of its higher activation energy (0.45 eV) compared to ions diffusion step (0.38eV)[14]. It also occurs at low temperatures but excess water under these conditions repassivates the interface according to eq. (4) and off sets it. From the C-V curves of these samples 5 h, 10 h, and 20 h it is evident that they show similar features but different in hysteresis loop widths and sizes of depletion regions which is in the order of 5 h> 10 h> 20 h. These results support for the hypothesis that the formation of ionic carriers is induced strongly by chained silanols, lower in degree by geminate silanols, and less affected by isolated silanols.

4. Summary

Electrical properties of mesoporous silica thin film are mainly affected by its inner surface properties such as concentration of silanol, type of silanol and adsorbed water. Not all of the silanol groups do the same electrical degradation on mesoporous silica thin film. Silanol groups in chains or at least coupled make porous

silicate to become hydrophilic, in turn enhance the formation of hydrogen-bonded systems with water molecules to increase orientational polarization and also leakage current. Isolated silanols are, on the contrary, hydrophobic and partially protect mesoporous thin film from moisture assault.

Acknowledgments

References

[1] G. Q. Lu and X. S. Zhao, "Nanoporous Materials Science and Engineering", Imperial College Press, London, p. 1, 2003.

[2] T. C. Chang, C. W.Chen, P. T. Liu, Y. S. Mor, H. M. Tsai, T. M. Tsai, S. T. Yan, C. H. Tu, T. Y. Tseng, and S. M. Sze, "Moisture-Induced Material Instability of Porous Organosilicate Glass", Electrochem. Solid-State Lett. Vol. 6, p. 13, 2003.

[3] Y. Uchida, S. Hishiya, N. Fujii, K. Kohmura, T. Nakayama, H. Tanaka, and T. Kikkawa, "Effect of moisture adsorption on the properties of porous-silica ultralow-k films", Microelectron. Eng., Vol. 83, p. 2126, 2006.

[4] A. P. Singh, P. Victor, P. G. Ganesan, O. Nalamasu, and G. Ramanath, "Moisture-induced capacitance-voltage instabilities in mesoporous silica thin films", Appl. Phys. Lett., Vol. 87, p.3506, 2005.

[5] a) H. Miyoshi, K. Yamada, K. Kohmura, N. Fujii, H. Matsuo, H. Tanaka, Y. Oku, Y. Seino, N. Hata, and T. Kikkawa, "Semiconductors-Theoretical Investigation of Dielectric Constant and Elastic Modulus of Three-Dimensional Isotropic Porous Silica Films with Cubic", Jpn. J. Appl. Phys., Vol. 44, p. 5982, 2005. b) H. Miyoshi, H. Matsuo, Yo. Oku, H. Tanaka, K. Yamada, N. Mikami, S. Takada, N. Hata, and T. Kikkawa, "Theoretical Analysis of Elastic Modulus and Dielectric Constant for Low-k Two-Dimensional Periodic Porous Silica Films", Jpn. J. Appl. Phys., Vol. 43, p. 498, 2004. c) H. Miyoshi, No. Hata, and T. Kikkawa, "Theoretical Investigation of Dielectric Constant and Elastic Modulus of Two-Dimensional Periodic Porous Silica Films with Elliptical Cylindrical Pores", Jpn. J. Appl. Phys., Vol. 44, p. 1166, 2005.

[6] I. Fisher, W. D. Kaplan, and M. Eizenberg, "Prediction of Survival in Follicular Lymphoma Based on Molecular Features of Tumor-Infiltrating Immune Cells", J. Appl. Phys., Vol. 95, p. 5762, 2004.

[7] S. Yu, T. K. S. Wong, X. Hu, and K. Pita, "Sol-gel derived mesoporous silica films used as low dielectric constant materials", Thin Solid Films, Vol. 462, p. 311, 2004.

[8] J. T. Luo, W. F. Wu, H. C. Wen, B. Z. Wan, Y. M. Chang, C. P. Chou, J. M. Chen, and W. N. Chen, "The roles of hydrophobic group on the surface of ultra low dielectric constant porous silica film during thermal treatment", Thin Solid Films, Vol. 515, p. 7275, 2007.

[9] S. Yang, P. A. Mirau, C. S. Pai, O. Nalamasu, E. Reichmanis, E. K. Lin, H. J. Lee, D. W. Gidley, and J. Sun, "Molecular Templating of Nanoporous Ultralow Dielectric Constant (≈1.5) Organosilicates by Tailoring the Microphase Separation of Triblock Copolymers", Chem. Mater., Vol. 13, p. 2762, 2001.

[10] D. Grosso, F. Cagnol, G. J. A. A. Soler-Illia, E. L. Crepaldi, H. Amenistsch, A. Brunet-Bruneau, A. Bourgeois, and C. Shanchez, "Fundamentals of Mesostructuring Through Evaporation-Induced Self-Assembly", Adv. Funct. Mater., Vol. 14, p. 310, 2004.

[11] P. Innocenzi, "Infrared spectroscopy of sol-gel derived silica-based films: a spectra-microstructure overview", J. Non-Cryst. Solids, Vol. 316, p. 309, 2003.

[12] D. H. Lee and H. D. Jeong, "Distinct clockwise capacitance-voltage hysteresis in aminopropyl- silsesquioxane thin films", J. Phys. Chem. C , Vol. 112, p. 16984, 2008.

[13] C. S. Kim and H. D. Jeong, "What originates the dielectric permittivity of silicate-silsesquioxane hybrid thin films?", J. Phys. Chem. B, Vol. 112, p. 16257, 2008.

[14] R. A. B. Devine, G. V. Herrera, "Electric-field-induced transport of protons in amorphous SiO_2", Phys. Rev., B, Vol. 63, p. 3406, 2001.

[15] a) L. Bollmann, V. N. Urade, and H. W. Hillhouse, "Controlling Interfacial Curvature in Nanoporous Silica Films Formed by Evaporation-Induced Self-Assembly from Nonionic Surfactants. II. Effect of Processing Parameters on Film Structure", Langmuir, Vol. 23, p. 4257, 2007. b) V. N. Urade, L. Bollmann, J. D. Kowalski, M. P. Tate, and H. W. Hillhouse, "Controlling Interfacial Curvature in Nanoporous Silica Films Formed by Evaporation-Induced Self-Assembly from Nonionic Surfactants. II. Effect of Processing Parameters on Film Structure", Langmuir, Vol. 23, p. 4268, 2007.