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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · JANUARY 2009

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What Originates the Dielectric Permittivity of Silicate-Silsesquioxane Hybrid Thin Films?

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Received: September 25, 2008; Revised Manuscript Received: November 02, 2008

Silicate-silsesquioxane or siloxane-silsesquioxane hybrid thin films are strong candidates as matrix materials for ultralow dielectric constant (low-k) thin films. We synthesized the silicate-silsesquioxane hybrid resins from tetraethoxyorthosilicate (TEOS) and methyltrimethoxysilane (MTMS) through hydrolysis and condensation polymerization by changing their molar ratios ([TEOS]–[MTMS] = 7:3, 5:5, and 3:7), spin-coating on Si(100) wafers. In the case of [TEOS]–[MTMS] = 7:3, the dielectric permittivity value of the resultant thin film was measured at 4.30, exceeding that of the thermal oxide (3.9). This high value was thought to be due to Si-OH groups inside the film and more extensive studies were preformed in terms of electronic, ionic, and orientational polarizations using Debye equation. The relationship between the mechanical properties and the synthetic conditions of the silicate-silsesquioxane precursors was also investigated. The synthetic conditions of the low-k films have to be chosen to meet both the low orientational polarization and high mechanical properties requirements.

Silicate-silsesquioxane or siloxane-silsesquioxane hybrid thin films have been investigated as promising materials for ultralow dielectric constant (low-k) thin films.^{1–4} In addition, they have also been regarded as one of the best matrix materials to provide nanoporous dielectrics for ultralow-k due to exceptional mechanical properties in terms of hardness and modulus as well as a low dielectric constant. The hybrid films have been synthesized using either a surfactant-templated approach or sol–gel polymerized resins.

Recently, we synthesized the silicate-silsesquioxane hybrid resins from tetraethoxyorthosilicate (TEOS) and methyltrimethoxysilane (MTMS) through hydrolysis and condensation polymerization (Figure 1) by changing their molar ratios ([TEOS]–[MTMS] = 7:3, 5:5, and 3:7), spin-coating on Si(100) wafers, and curing at 450 °C in vacuum to give low-k dielectric thin films of good uniformity. The resultant thin films fabricated from the synthetic conditions ([TEOS]–[MTMS] = 7:3, 5:5, and 3:7) are labeled sample **I**, sample **II**, and sample **III**, respectively. Here, the silicon atoms of the quartet structure (Q) in the TEOS molecules have been thought to give higher modulus and hardness values confirmed by the nanoindentation results (Supporting Information Figure S1). Conversely, the methyl groups in the MTMS molecules having the silicon atom of the triplet structure (T) have been known to provide not only solution processability but also low-k values due to their intrinsic, molecular free volume, and low polarization in the resultant dielectric thin films. The synergetic function of two kinds of silicon structures in the silicate-silsesquioxane hybrids was believed to make them one of most promising candidate materials for low-k applications. The dielectric permittivity values of the hybrid thin films were investigated in metal–insulator–semiconductor (MIS) structures using an HP4284 LCR meter (Supporting Information Figure S2). As the higher molar

concentration of the MTMS in the syntheses of the hybrid resins was used, lower dielectric permittivity values were obtained for the resultant thin films (Supporting Information Table S1 and Figure S3). This is due in part to the methyl groups in the MTMS giving rise to molecular free volumes in the films, as previously expected. However, there was significant concern for the case of sample **I**, where the dielectric permittivity value of the resultant thin film was measured at 4.30, exceeding that of the thermal oxide (3.9),⁵ and is believed to be higher than that of any other carbon-doped silicon oxide (SiOC) because of its highest density. This high value was initially thought to be due to Si-OH groups inside the film, but more extensive studies are required to ascertain its true nature.

In order to investigate the physicochemical origins causing the dielectric permittivity values in our silicate-silsesquioxane thin films, a more systematic and fundamental approach for the investigation of the dielectric properties was required beyond the conventional electrical engineering knowledge for measuring only the dielectric permittivity; in material science or electrical engineering fields, the word “dielectric constant” is conventionally used instead of the word “dielectric permittivity”. It is the contention of the authors that the physicochemical theoretical framework based on the Debye theory will support this scientific agenda.^{6–9} Originally, the dielectric permittivity of a material is proportional to its polarization, which is divided mainly into electronic, ionic, and orientational. Among them, electronic polarization is related to the distortion of electron clouds within the atom as the polarity of applied electric field is changed, while ionic polarization is due to the fluctuation of electron clouds through chemical bonds. Under an alternating electric field of relatively higher frequency ($>10^{11}$ Hz), only two polarization mechanisms can occur. Furthermore, for typical visible light (633 nm or 4.74×10^{14} Hz) in the far higher frequency ranges, only electronic polarization occurs. On the contrary, in low frequency ranges below 10^{11} Hz, orientational

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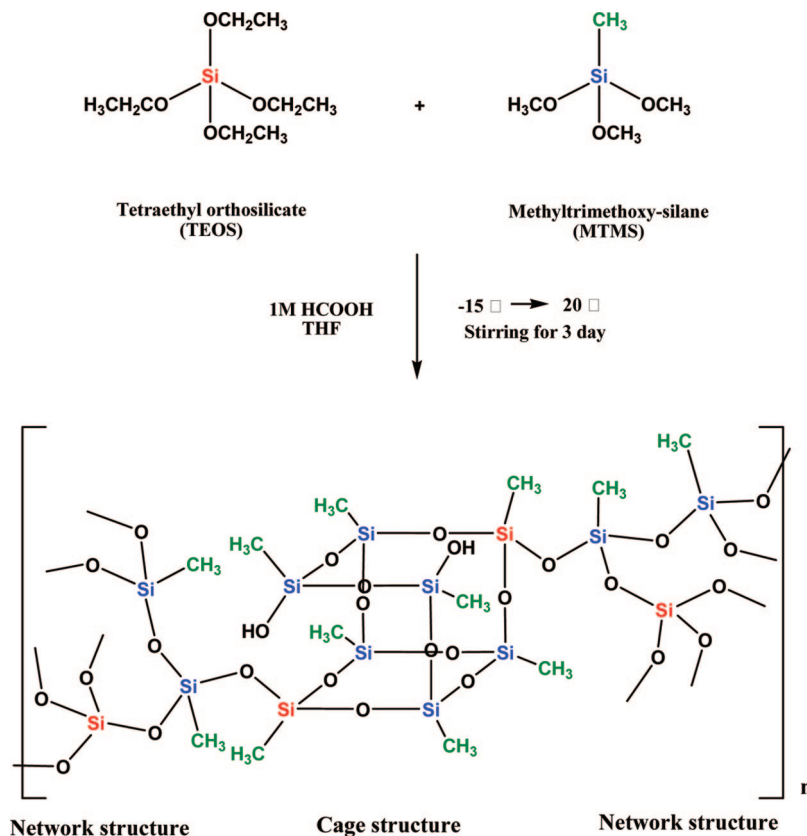


Figure 1. Schematic of hydrolysis and condensation polymerization with TEOS and MTMS.

polarization is added to the two polarizations and invoked by an orientational response of permanent dipole moments to the alternating electric field. Therefore, within the frequencies of 10 kHz~1 MHz typically used to determine the dielectric permittivity of low-k thin films, all three polarization mechanisms have to be counted. These arguments can be realized quantitatively through the following Debye equations:⁶⁻⁸

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \left(\frac{4\pi\rho\mu_0^2}{9k} \right) \frac{1}{T} + \frac{4\pi\alpha\rho}{3} \quad (1)$$

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi\alpha\rho}{3} \quad (2)$$

where ε denotes the (static) dielectric permittivity and ε_∞ is the high-frequency dielectric permittivity. The values μ_0 , α , ρ , k , and T correspond to the permanent dipole moment, distortion polarizability, number density of the permanent dipole, the Boltzmann constant, and temperature (Kelvin), respectively. On the right part of (eq 1), the first term indicates the contribution of the orientational polarization to the dielectric permittivity, while the second term accounts for the contribution of distortion polarization consisting of electronic and ionic polarizations, which can be used to give ε_∞ according to (eq 2). Then, ε is measured with increasing temperature and the contribution of orientational and other polarizations can be easily obtained. In order to apply these arguments toward our silicate-silsesquioxane thin films, we measured the dielectric permittivity values with increasing temperature in the range of 30~170 °C (Figure 2). From these data, we can draw the graphs in which the $(\varepsilon - 1)/(\varepsilon + 2)$ values are plotted according to reciprocal temperature ($1/T$) (Figure 3a and Supporting Information Figure S4). Here,

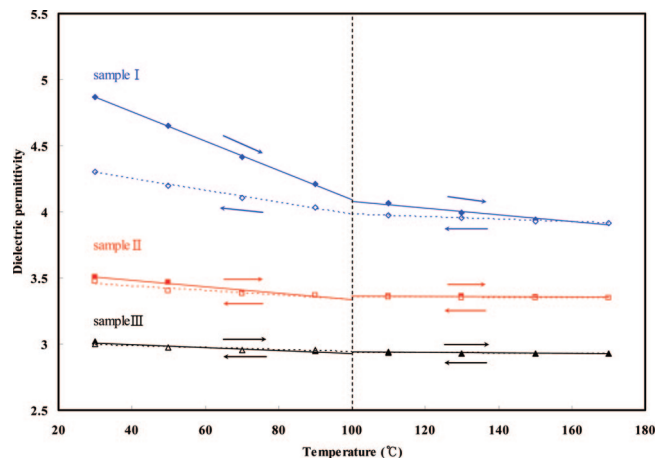


Figure 2. Dielectric permittivity values with increasing temperature between 30~170 °C for the three low-k thin films ([TEOS]-[MTMS] = 7:3, 5:5, and 3:7). The resultant thin films fabricated from the synthetic conditions ([TEOS]-[MTMS] = 7:3, 5:5, and 3:7) are labeled sample I, II, and, III, respectively.

in the case of sample I, there is an abrupt change in the slope at 100 °C, which corresponds to the boiling point of water. In addition, in the low temperature range of 30~90 °C, the slopes of the graphs are very different according to the direction of the temperature change. To explain these experimental results, we propose that this is attributed to the weakly physisorbed water molecules that are so different from the Si-OH groups in terms of intermolecular interactions. The weakly physisorbed water molecules are outgassed from the films at 100 °C, while below 100 °C the water molecules from the atmosphere are absorbed onto the thin films and changed to the weakly physisorbed water state. Thus, this kind of molecule is reversible with changing temperature in terms of adsorption and desorption

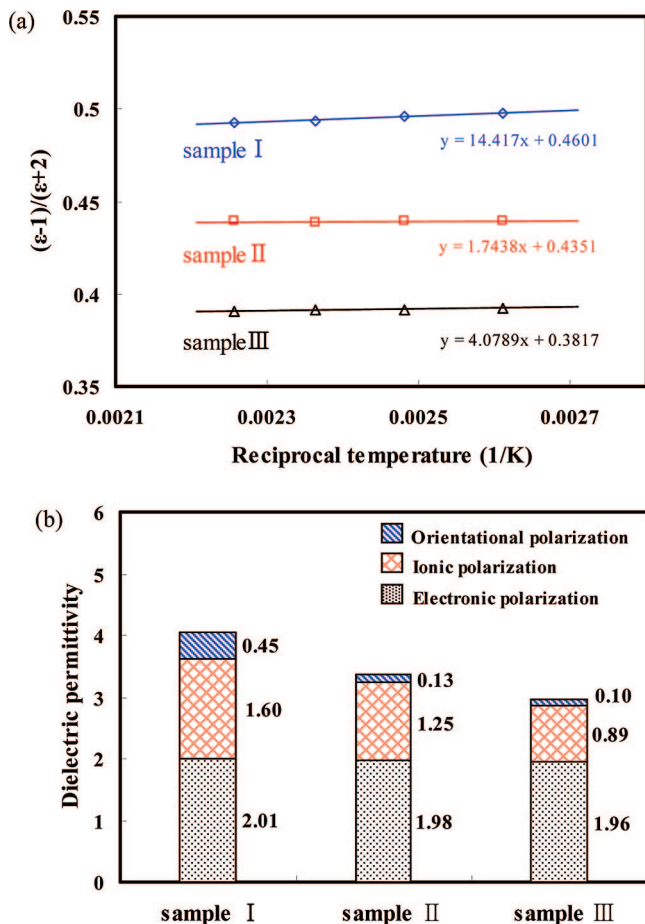


Figure 3. (a) The y-intercept values and slopes in the fitted equations, representing the Debye equation (eq 1), were determined between 110~170 °C (especially, with decreasing temperature). (b) Allocation of the dielectric permittivity values in terms of the three polarization mechanisms for the three low-k thin films (sample I, II, and, III) between 170~110 °C (especially, with decreasing temperature).

on the films. Because the dielectric permittivity of the water molecules in the liquid state is as high as 78.5,⁶ the existence of the weakly physisorbed water molecules makes the accurate and reproducible measurement of the dielectric permittivity at room temperature very difficult. These tendencies are repeated for other cases of sample II and sample III. In this letter, we wish to focus on a high temperature range of 110~170 °C (especially, with decreasing temperature) (Figure 3a,b) with analyses of the other conditions also performed and compared to validate this simplification (Supporting Information Figure S6). This is because the absorption and desorption processes of the weakly physisorbed water molecules within the low temperature range of 30~90 °C are much too dependent upon experimental conditions such as humidity, temperature stay time, temperature change rate, and direction of temperature change, thus requiring a more sophisticated and controlled apparatus and thereby precluding reproducibility of dielectric permittivity values in this stage. Then, the y-intercept values and slopes in the fitted equations, representing (eq 1), were determined only in the temperature range of 110~170 °C. The ϵ_{∞} values were calculated from the y-intercept of the fitted equation using (eq 2), with ϵ values calculated by substituting 303.15 K for T in the equation. Here, we can obtain the orientational polarization ($\epsilon_{\text{orientational}}$) from the following equation:

$$\epsilon_{\text{orientational}} = \epsilon - \epsilon_{\infty} \quad (3)$$

In the case of sample I, $\epsilon_{\text{orientational}}$ was estimated to be 0.45 (11% of total the dielectric permittivity 4.06), while in the case of sample III, it decreased to 0.10. The higher orientational polarization might be due to the existence of Si-OH groups in our silicate-silsesquioxane thin films, which has been mentioned in previous studies on low-k.⁹⁻¹¹ To verify this possibility, FT-IR spectra for our thin films were obtained (Supporting Information Figure S7). From reviewing previous reports and comparing them with our experimental results, we can conclude that the stretching frequencies of the physisorbed water molecules and the Si-OH groups are different.¹²⁻¹⁴ Within the range of 3600~3800 cm^{-1} , the two peaks of about 3775 and 3700 cm^{-1} are attributed to free Si-OH groups and the peak at about 3635 cm^{-1} is attributed to hydrogen-bonded Si-OH group. On the other hand, the peak at about 3430 cm^{-1} is ascribed to the different hydrogen-bonded Si-OH group and weakly physisorbed water molecules. As the [TEOS]-[MTMS] ratio increased, we could see the higher peak intensity in the three Si-OH stretching vibrations in the range of 3600~3800 cm^{-1} , indicating that the Si-OH could be the origin of the orientational portion of the dielectric permittivity values. This can be confirmed by the graph showing a good relation between $\epsilon_{\text{orientational}}$ and the area of the three prominent peaks in the FT-IR spectra (Supporting Information Figure S8). On the contrary, the peak intensity of the 3435 cm^{-1} is not significantly changed with varying the [TEOS]-[MTMS] ratio (Supporting Information Figures S7 and S8). This implies that the hydrogen-bonded Si-OH groups or the weakly physisorbed H_2O molecules might not significantly contribute to the ϵ values in the temperature range of 110~170 °C. This is thought because the amount of the hydrogen-bonded Si-OH groups is very small and the physisorbed H_2O molecules could easily evaporate from the thin films heated above 100 °C. Necessarily, there is no strong correlation between the area of the peak at about 3430 cm^{-1} and the orientational polarization (Supporting Information Figure S8). It seems unusual that for sample I, the dielectric constant (4.30) measured at room temperature is significantly higher compared to that (4.06) estimated from the fitted equation between 110~170 °C though the amount of the weakly physisorbed water molecules is far less than that of Si-OH groups. This discrepancy can be resolved by the concept of dielectric friction on a rotating molecule. In the Si-OH groups, some of rotational degrees of freedom are hindered due to their geometrical constraints, thereby decreasing the effective dipole moment. On the contrary, in the weakly physisorbed H_2O molecules, molecular rotation is less hindered and the relatively low concentration of the latter can contribute largely to the dielectric permittivity.

The value ϵ_{∞} is divided into ϵ_{ionic} and $\epsilon_{\text{electronic}}$, where $\epsilon_{\text{electronic}}$ was calculated from the refractive index (n) value at 632.8 nm, according to $\epsilon_{\text{electronic}} = n^2$.¹⁵ The n value was obtained using spectroscopic ellipsometry (Supporting Information Figure S5). Then, ϵ_{ionic} can finally be estimated from the following equation:

$$\epsilon_{\text{ionic}} = \epsilon_{\infty} - \epsilon_{\text{electronic}} \quad (4)$$

The $\epsilon_{\text{electronic}}$ were not significantly affected with changing of the mole ratio of TEOS and MTMS precursors in the syntheses of the resins, indicating no significant changes in atomic skeletal density of the resultant dielectric films (Figure 3b). One the other hand, ϵ_{ionic} decreased largely from 1.60 for sample I, to 1.25 for sample II and 0.89 for sample III. This decrease in the ionic polarization is related to the decrease of the [TEOS]/[MTMS] ratio, resulting in the decrease [Q]/[T] ratio in silicon atoms of the films with surely guessed from the FT-IR results

(Supporting Information Figure S7).¹⁶ This is due to the Si–O bond involved with the silicon atoms of the Q structure being more ionic than the Si–C bond attached to the silicon atoms of the T structure.

The significant contribution of permanent dipoles such as Si–OH groups and physisorbed H₂O molecules in the 450 °C-cured silicate-silsesquioxane thin films is undesirable not only for lowering the dielectric permittivity but is also risky for the reliability of the device into which the low-k dielectric thin films are applied. For example, the Si–OH groups in the film can induce higher moisture absorption in the chip integration process, resulting in, “via poisoning” problem, intermetal dielectric (IMD) layers in semiconductor chips.^{17–20} Then, it is wholly possible that the synthetic chemistry for the low-k precursor resins has to be designed to decrease electrical defect structures such as Si–OH, because any additional surface modification processes for IMD fabrication (NH₃ or H₂ plasma treatments^{19–20}) cannot allow those kind of defect structures to be removed completely. This is because the process conditions have to be kept below a certain intensity to maintain the low dielectric permittivity values (a harsh process condition densifies the low-k films, resulting in the increase in dielectric permittivity).

To date, this is the first concrete investigation into the origins of the dielectric permittivity of silicate-silsesquioxane hybrid thin films where the dielectric permittivity is analyzed in terms of electronic, ionic, and orientational polarizations. This physicochemical view of low-k thin films needs to be expanded more to help not only synthetic chemists and material scientists to design custom low-k dielectric materials of high performance, but also process engineers to select exclusive low-k candidates and improve the electrical reliability of the IMD structures using these films.

Acknowledgment. This work was financially supported by the Chonnam National University.

Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JP808529Q