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Distinct Clockwise Capacitance–Voltage Hysteresis in Aminopropyl-silsesquioxane Thin Films

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Aminopropyl-silsesquioxane resins and thin films were synthesized from aminopropyltrimethoxysilane (APTMS). To investigate the changes in the molecular structure of the film with increasing curing temperature, Fourier transform infrared spectroscopy (FT-IR) was performed. The dielectric properties of the thin films were investigated by capacitance–voltage (C–V) measurements in a metal–insulator–semiconductor (MIS) structure. To explain the spectral changes in the FT-IR results, it is proposed that the Si–OH and aminopropyl groups freely exist without hydrogen bonding interactions in the curing temperature range 100–200 °C, while molecular structures such as $\text{N}(\text{Si}\equiv)_3$, $\text{N}(\text{Si}\equiv)_2$, and $\text{O}(\text{Si}\equiv)_2$ are formed at higher temperatures in the range 250–300 °C. The dielectric constant values and dissipation factors are regarded as being suitable for electronic applications, e.g., the gate insulators of organic thin film transistor (OTFT) devices. Interestingly, amphoteric charge trap behavior, such as a distinct clockwise C–V hysteresis, was observed in the sample cured at 300 °C. It is proposed that this originates from the coexistence of $\text{N}(\text{Si}\equiv)_2$ and E' centers in the cured films, into which positive charges or negative charges originating from the metal gate electrode are trapped, depending on the polarity of the applied electric field. It seems that the nitrogen-related molecular defects act as electron trap centers in the aminopropyl-silsesquioxane thin films.

Introduction

Organic thin film transistors (OTFTs) have drawn much interest for their application to active matrix displays,^{1,2} sensors,³ and radio frequency identification (RFID) tags⁴ because they have fundamental advantages, such as low temperature processibility, low cost, and applicability to flexible electronics, compared with conventional Si technology. Considering the operating principles of OTFTs in terms of device physics, it is obvious that, to realize high quality OTFTs, organic semiconductors of high charge mobility are not the only critical component, but that it is also very important to incorporate a suitable gate insulator.⁵

Organic–inorganic hybrid materials are strong candidates for solution-processed gate insulators which enable the fabrication of low-cost and high-performance OTFTs. As a class of organic–inorganic hybrid materials, sol–gel polymerized siloxane or silsesquioxane materials, which consist of inorganic and organic components bonded on the molecular level and have the merits of both SiO_2 and organic polymers, have been widely investigated. The dielectric constants, refractive indexes, thermal stabilities, and hydrophobicities of films made with these materials can be easily tuned by selecting suitable monomers and optimizing the sol–gel polymerization and the film deposition process conditions. For example, Bao et al. first investigated the use of silsesquioxane films as gate insulators for OTFTs.⁶ The spin-coated low-molecular-weight precursors had a molecular formula of $\text{RSiO}_{1.5}$, where R can be a hydrogen, alkyl, alkenyl, alkoxy, or aryl group. The silsesquioxane films spin-coated from the precursors were cured at temperatures below 150 °C, and the resulting film morphology was strongly dependent on the substrate and processing conditions. On the other hand, Choi et al. reported an interesting organic–inorganic hybrid approach to demonstrate solution-processed gate insulators. They synthesized methacrylate hybrid materials using

methacryloxypropyltrimethoxysilane (MPTMS), which are photopatternable and solution-processable for OTFTs.⁷ Alternatively, poly(methylsilsesquioxane) materials, which were tested as a modification agent for the gate dielectric surface, provided significantly improved performance in polythiophene-based organic thin film transistors.^{8,9} It was reported that this was because the high concentration of methyl groups renders the dielectric surface more hydrophobic, thereby facilitating the molecular ordering of the polythiophene layer by reducing the charge localization at the interface between the organic semiconductor and the gate insulator.¹⁰

Recently, we investigated the synthesis and dielectric properties of a new type of silsesquioxane film for use as the solution-processed gate insulator for low temperature processed OTFTs. These films were made by the spin-coating of silsesquioxane resins which were synthesized from aminopropyltrimethoxysilane (APTMS) and methyltrimethoxysilane (MTMS) precursors by the sol–gel polymerization reaction. The amine groups in the APTMS molecule act as a base catalyst in the hydrolysis and co-condensation polymerization. In the synthesized aminopropyl-silsesquioxane resins, the inorganic components consisting mainly of –Si–O– moieties are thought to be responsible for the mechanical and electrical stabilities of the final cured films, while the organic components consisting of –CH_3 and $\text{–CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ groups are thought to be responsible for their solution processability.

Though the films have not yet been incorporated into OTFT devices, their dielectric properties, such as their dielectric constant and dissipation factor, are likely to be regarded as promising for gate insulator applications. Unfortunately, there were unexpected results, namely the observation of a distinct clockwise hysteresis in the capacitance–voltage (C–V) measurements for the film cured at 300 °C, indicating significant trapping of negative charges, which is not desirable for the gate application of OTFT devices. In this article, we mainly focused on the investigation of the physicochemical origin for the unusual charge trap phenomenon, for which we propose the

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formation of Si–N bonds in the curing mechanism of the aminopropyl-silsesquioxane thin films.

Experimental Section

The syntheses of aminopropyl-silsesquioxane resins were performed at room temperature in a closed vial in an air atmosphere. A 1.36 g (0.010 mol, Aldrich, 98%) sample of methyltrimethoxysilane (MTMS) was dissolved in 4.60 g of ethanol and 0.60 g (0.0033 mol, Aldrich, 97%) of aminopropyltrimethoxysilane (APTMS) was added. Then, 0.18 g (0.010 mol) of H₂O was slowly added to this solution under vigorous stirring at room temperature. The final mole ratio of MTMS:APTMS:H₂O in the solution was 3:1:3. Finally, the solutions were stirred for 5 min at room temperature in an air atmosphere, providing sol solutions of the aminopropyl-silsesquioxane resins. After filtering the sol solutions using a filter (PTFE, 0.25 μ m), they were spin-coated on a p-type Si(100) wafer (resistivity 1–30 Ω ·cm; thickness 525 nm) at 2000 rpm. The Si wafers were purchased from Silicon Valley Microelectronics, Inc., and the resistivity and thickness values were also obtained from the same company. Then, the films were heated at 80 °C on a hot plate for 10 min in an air atmosphere to remove the remaining solvents. Finally, the films were cured for 30 min at temperatures of 100, 200, 250, and 300 °C on a hot plate in an air atmosphere. The curing temperatures were measured by a thermocouple equipped in the hot plate. In order to investigate the compositional change with increasing curing temperature, X-ray photoelectron spectroscopy (XPS) measurements were conducted on a MultiLab 2000 (Thermo Electron Corp., England) spectrometer under a pressure below 1×10^{-9} Torr with an Al K α X-ray source at passing energy of 50 eV. A 2 keV Ar⁺ ion gun sputtering of 5 min was used for depth profiling or brief cleaning of the surface of the samples prior to the XPS measurements. Fourier transform infrared spectroscopy (FT-IR) was implemented to investigate the molecular structure of the aminopropylsiloxane films as a function of the curing temperature. The measurements were conducted on a Bruker IFS66v/S spectrometer which was operated under 3 mbar in the mid-IR range from 4000 to 400 cm⁻¹, and all of the spectra were obtained at a spectral resolution of 2 cm⁻¹ in transmittance mode. Metal–insulator–semiconductor (MIS) device structures were fabricated to investigate the capacitance–voltage (C–V) characteristics. Aluminum metal with a thickness of 300 nm and a diameter of 0.55 mm was deposited on the aminosilsesquioxane thin films by the thermal evaporation technique and served as a top electrode. Here, the thickness and diameter values of the aluminum electrode were measured from field-emission scanning electron microscope (FE-SEM) images. The back side of the silicon wafer in the MIS devices was also coated with aluminum metal to diminish the contact resistance. Using an HP4284 LCR meter, the C–V measurements were obtained by applying an ac voltage with a frequency of 1 MHz and an amplitude of 100 mV to the top aluminum electrode, and a dc bias voltage was swept over the ranges of –10 to 10 V and –30 to 30 V. C–V curves were acquired in both forward and reverse directions, and afterward, these were compared with each other to study the charge trap mechanisms. A metal–insulator–metal (MIM) device structure was also fabricated to investigate MIM C–V characteristics of the 300 °C cured film. The MIM structure was prepared on a Si(100) wafer. In order to isolate the MIM structure electrically, the silicon wafer was thermally oxidized, giving a 3000 Å SiO₂ layer. Then, titanium metal of 200 Å was deposited as adhesion layer and platinum metal was deposited as the bottom electrode, whose thickness was

TABLE 1: Results of the Compositional Analysis (atom %) of the Aminopropyl-silsesquioxane Thin Films Obtained Using XPS

	curing temperature			
	100 °C	200 °C	250 °C	300 °C
carbon	38	38	31	29
oxygen	34	35	40	42
nitrogen	4	4	2	1
silicon	24	23	27	28

measured as 2000 Å in an FE-SEM inspection. After the 300 °C cured aminopropyl-silsesquioxane thin film was formed on the platinum electrode, gold metal with thickness of 3000 Å was deposited as the top electrode, completing the MIM structure of Au/dielectric/Pt/Ti/SiO₂/Si(100).

Results and Discussion

The results of the compositional analysis of the aminopropyl-silsesquioxane thin films obtained using XPS are summarized in Table 1. The relative concentrations of carbon and nitrogen elements is significantly decreased at a curing temperature of 250 °C compared with those of oxygen and silicon. This indicates that the aminopropyl groups are decomposed and degassed out of the films at 250 °C. Most of the methyl groups are thought to remain, because their half-life is known to be more than 100 000 times longer than that of the propyl group at 250 °C in air.¹¹

The FT-IR spectra of the aminopropyl-silsesquioxane thin films cured at the various temperatures are shown in Figure 1. As shown in Figure 1a, in the case of the thin films cured at 100 and 200 °C, the absorption peak at 3438 cm⁻¹ is attributed to the stretching of Si–OH and the peaks at 3359 and 3290 cm⁻¹ are attributed to the asymmetric stretching and symmetric stretching of –NH₂, respectively.¹² If there were a significant amount of hydrogen bonding interactions between the NH₂ and Si–OH groups, these two absorption peaks would not be detected.¹² Hence, the presence of the three distinct peaks undoubtedly indicates the absence of hydrogen bonding interactions between these two groups in the samples cured at 100 and 200 °C. This denotes that the Si–OH and aminopropyl groups exist freely under these curing conditions; refer to structure **I** of Figure 2a for clear visualization. In the spectrum of the sample cured at 250 °C, the Si–OH stretching peak at 3438 cm⁻¹ is no longer clearly observed but could still be present with decreased intensity, masked by stronger peaks on each side. The NH₂ stretching peaks at 3359 and 3290 cm⁻¹ still remain with some peak broadening. This is likely due to the elimination of H₂O molecules accompanying the formation of the Si–N bonds (which gives rise to the peak at 846 cm⁻¹; see below), as proposed with respect to structure **II** of Figure 2a. In the spectrum of the sample cured at 300 °C, the peaks related to the NH₂ stretching are not clearly visible and, instead of them, broad peaks appear at 3500 and 3404 cm⁻¹. Therefore, these new peaks can be related to structure **V**, **VI**, or **VII** which are formed from structure **II**, as shown below.

As shown in Figure 1b, in the spectra of the thin films cured at 100 and 200 °C, the absorption peaks at 2966, 2931, and 2871 cm⁻¹ are due to alkyl groups such as propyl and methyl groups bonded to the silicon atoms in the films. In the case of the samples cured at 250 and 300 °C, the absorption intensity of the 2931 and 2871 cm⁻¹ peaks are significantly decreased, which is interpreted as being due to the elimination of the propyl groups, as proposed in Figure 2b. In addition, the intensity of

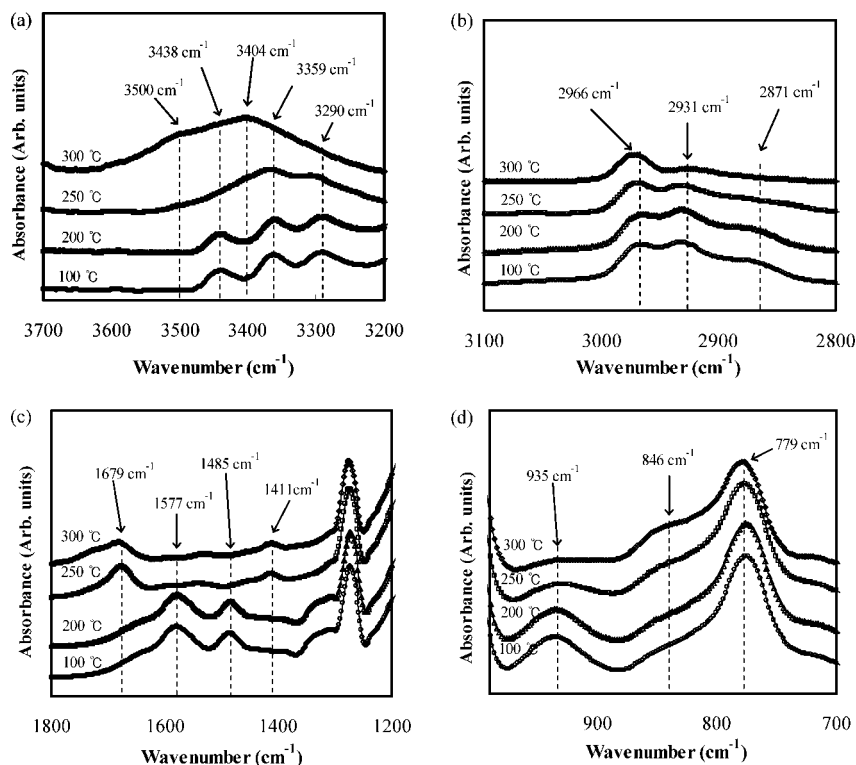


Figure 1. FT-IR spectra of the aminopropyl-silsesquioxane thin films cured at various temperatures in the ranges (a) 3700–3200, (b) 3100–2800, (c) 1800–1200, and (d) 1000–700 cm^{-1} .

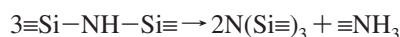
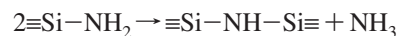
the 2966 cm^{-1} peak is not significantly decreased compared with those of the former two peaks. This is because this peak is attributed in part to the methyl groups, as mentioned already above, whose half-life is known to be more than 100 000 times longer than that of the propyl group at 250 $^{\circ}\text{C}$ in air.¹¹

As shown in Figure 1c, in the spectra of the thin films cured at 100 and 200 $^{\circ}\text{C}$, peaks at 1577 cm^{-1} due to the N–H scissoring vibration and at 1485 cm^{-1} due to $-\text{NH}_3^+$ deformation are also observed, confirming the existence of $-\text{NH}_2$ and $-\text{NH}_3^+$ groups inside the films.¹² Because the $-\text{NH}_3^+$ groups have no lone pair electrons, they cannot directly attack the neighboring Si atoms. However, the $-\text{NH}_3^+$ groups can be deprotonated to participate in the Si–N bond formation with respect to Le Chatelier's principle. This is why none of the proposed structures has an $-\text{NH}_3^+$ group. These two peaks completely disappeared in the spectra of the thin films cured at 250 $^{\circ}\text{C}$. In a previous paper on APTMS thin films, the absence of these two peaks was interpreted as indicating the occurrence of a polymerization reaction leading to the formation of new molecular structures.¹² A similar reaction, a dimerization, is thought to occur in the curing process of our films. The new peak at 1679 cm^{-1} observed in the spectra of the samples cured at 250 and 300 $^{\circ}\text{C}$ is interpreted as C=C stretching of propylene grafted to silicon atom, which is explained by suggesting the formation of a new molecular structure, such as structure **III** in Figure 2b. This is because the free C=C stretching vibrations of pure propylene appear at 1665 cm^{-1} .¹³ C–H stretching peaks of structure **III** are likely to be related to the 2931 cm^{-1} peak in the Figure 1b. The other nonolefinic peaks are not distinctively in our spectra. Moreover, another new peak at 1411 cm^{-1} appeared concurrently with the 1679 cm^{-1} peak in the spectra of the samples cured at 250 and 300 $^{\circ}\text{C}$. This peak has not yet been interpreted completely for our thin films, though it has been assigned to vinyl groups grafted to siloxane structures.¹⁴

As shown in Figure 1d, significant changes in the peaks at 935 and 846 cm^{-1} were observed with increasing curing

temperature. The decrease in the intensity of the former peak is related to the disappearance of the $-\text{Si}-\text{OH}$ groups in the films, as mentioned in the discussion of Figures 1a and 2a. The increase in the absorption intensity of the latter peak in the spectra of the samples cured at 250 and 300 $^{\circ}\text{C}$ is attributed to the formation of a new molecular structure related to the Si–N bonds, because in a study of silicon nitride films synthesized from polydimethylsilane and NH_3 at 400 $^{\circ}\text{C}$, the peak at 835 cm^{-1} was assigned to distorted-pyramidal N geometries, where a nitrogen atom is bonded to three silicon atoms.¹⁵ Hence, we wish to assert that the absorption peak at 846 cm^{-1} can be explained by structure **V** shown in Figure 2c. The difference in the peak positions of 11 cm^{-1} is likely due to the different distortions of the two pyramidal N geometries. On the other hand, the 846 cm^{-1} peak appears to be present with lower intensity even in the 100 and 200 $^{\circ}\text{C}$ cured samples. This indicates the possibility that the Si–N bonds and structure **V** still exist in the 100 and 200 $^{\circ}\text{C}$ cured samples. Therefore, it could be also said the Si–N bonds inducing structure **V** become more abundant with increasing curing temperature.

In the pyrolysis reaction of polysilazane in the range 200–500 $^{\circ}\text{C}$, $\equiv\text{Si}-\text{NH}_2$ groups were reported to condense through transamination reactions, leading to the cross-linking of the chains through the formation of Si–N–Si bridges.¹⁶ These are provoked by the attack of the lone pair electrons of the nitrogen atoms on the vacant 3d orbital of the silicon atoms, as follows.



In a similar way, as shown in Figure 2b, we can first propose a cyclic reaction which is also triggered by the attack of the lone pair electrons of the nitrogen atom on the vacant d orbital of another silicon atom, which is connected to the propylene bridge, via an intermediate state consisting of a five-membered ring, producing either structure **III** or structure **IV**. Then, as in

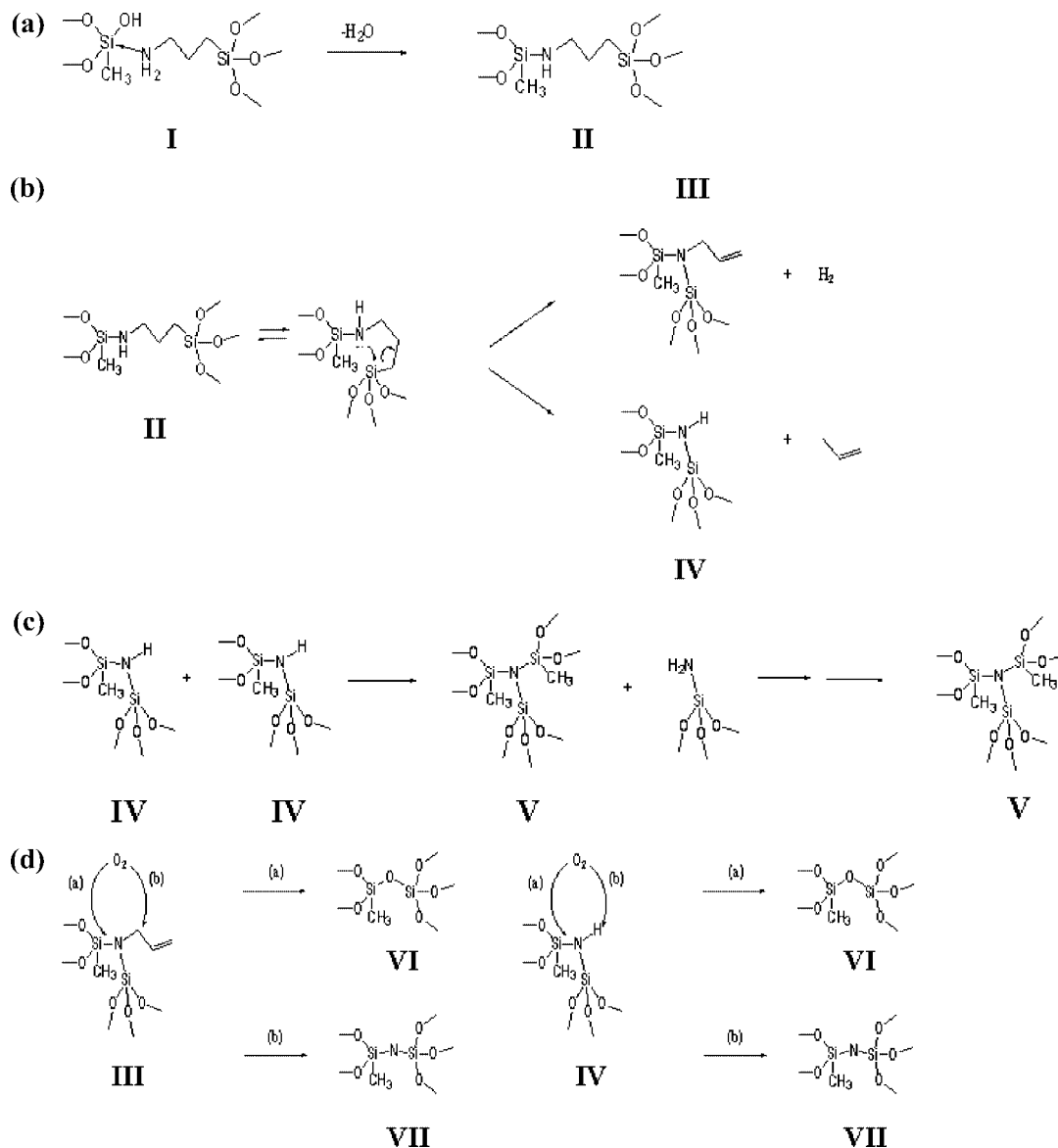


Figure 2. Tentatively proposed curing mechanism: (a) formation of Si–N bond at the step of 200 \rightarrow 250 $^{\circ}\text{C}$, (b) elimination reactions via a five-membered intermediate, (c) transamination reaction, and (d) exchange reaction and formation of $\text{N}(\text{Si}\equiv)_2$ (structure II, viz., $\text{N}(\text{Si}\equiv)_2$) in the range 250–300 $^{\circ}\text{C}$. In (d), the arrows show the direction of oxygen attack, not electron flow.

the case of polysilazane, structure IV undergoes a transamination reaction to give rise finally to only structure V, as shown in Figure 2c.

Additionally, it is also proposed that structure III or structure IV further reacts with O_2 molecules in the air at ambient pressure in the temperature range 250–300 $^{\circ}\text{C}$, producing either structure VI or structure VII, according to the direction of the O_2 attack, as shown in Figure 2d. The former type of reaction in which the nitrogen atom is exchanged with the oxygen atom is quite thermodynamically favorable, because the Si–O bond is stronger than the Si–N bond. Thus, we could say that structures V, VI, and VII are all forming at 300 $^{\circ}\text{C}$, depending on the availability of oxygen. Furthermore, we cannot exclude the possibility that the two silicon atoms in structure VI are separated from each other, forming a kind of defect structure such as $\{\equiv\text{Si}-\text{O}^{\cdot} + \cdot\text{Si}\equiv\}$, because the local bonding geometries are significantly distorted by the mechanical strains accumulated during the curing process. This phenomenon has been observed in spin-on glass (SOG) with high tensile stress.¹⁷ The rationale for structure V is discussed later (see below).

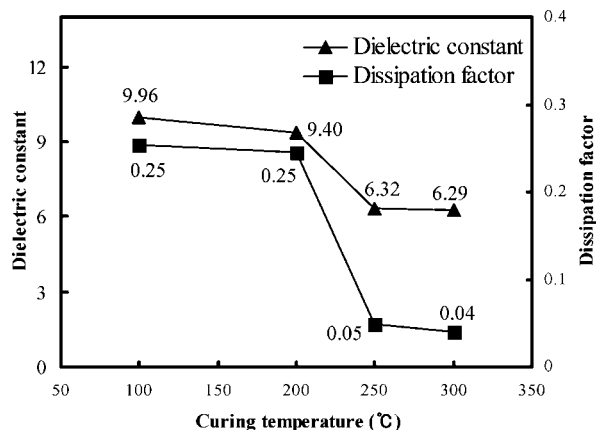


Figure 3. Changes in the dielectric constant and dissipation factor of the thin films with increasing curing temperature.

Figure 3 shows the changes in the dielectric constant and dissipation factor of the thin films with increasing curing temperature, which were measured in the MIS device. The

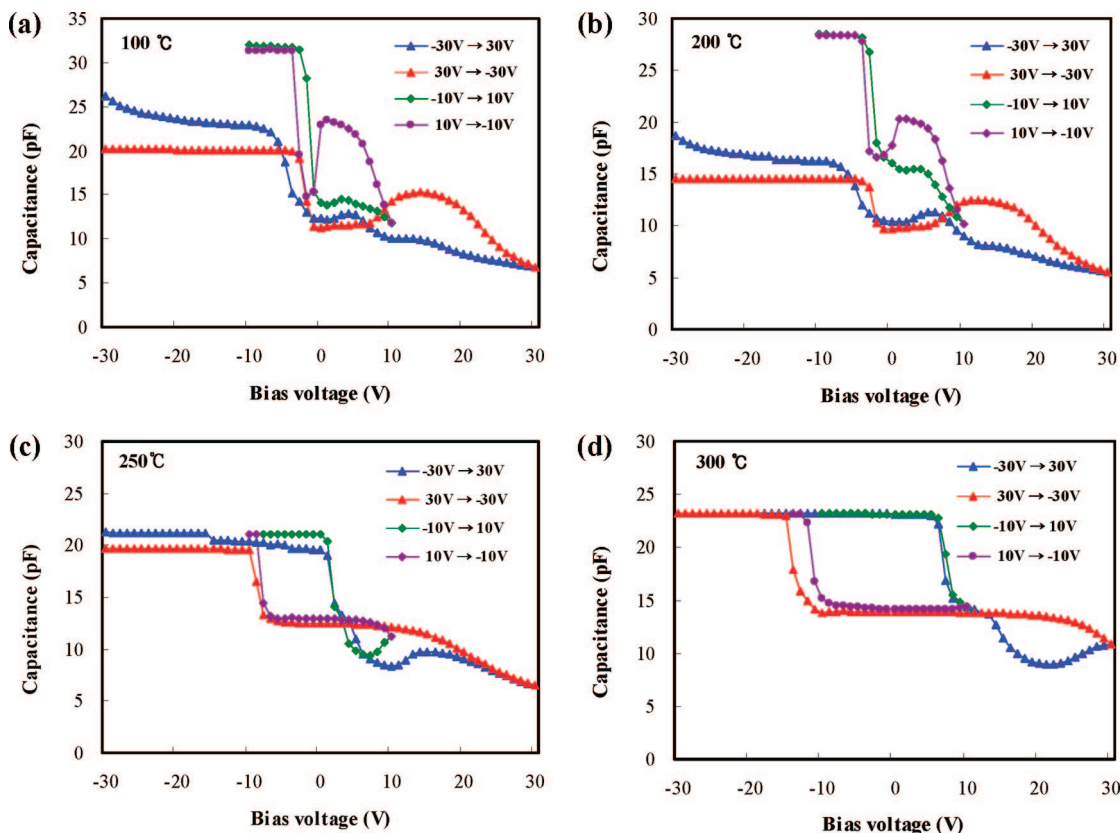


Figure 4. C–V characteristics according to curing temperature: (a) 100, (b) 200, (c) 250, and (d) 300 °C. The characteristics abruptly change as the curing temperature is increased from 200 to 250 °C.

dielectric constants of the films cured at 250 and 300 °C were 6.32 and 6.29, respectively, which were lower than the values of 9.96 for the sample cured at 100 °C and 9.40 for the sample cured at 200 °C. This is due to both the disappearance of the Si–OH groups and $-\text{NH}_2$ groups and the formation of new molecular structures assigned to the $\text{N}(\text{Si}\equiv)_3$ and $\text{O}(\text{Si}\equiv)_2$ bonding geometries at the higher curing temperatures, which are discussed in relation to the above FT-IR results. This is because the Si–OH groups and $-\text{NH}_2$ groups give rise to a higher dielectric constant via the orientational polarization mechanism, while the others do not. When the frequency of applied voltage is low ($<10^{11}$ Hz), the permanent dipoles such as $-\text{O}^{\delta-}-\text{H}^{\delta+}$ or $-\text{N}^{\delta-}-\text{H}^{\delta+}$ can change direction fast enough to follow the change in direction of the applied field.¹⁸ It results in additional contribution to polarization and the dielectric constant, which is defined as orientational polarization. In a dielectric thin film, the contribution of the orientational polarization to its dielectric constant can be analyzed in a quantitative manner by using the Debye equation,¹⁸ which will be demonstrated for our silsesquioxane thin films and published later. Moreover, the abrupt decrease in the dissipation factor in Figure 3 is also explained by the same phenomenon.

Figure 4 shows the C–V curves according to the curing temperature. It is noteworthy that the C–V results abruptly change as the curing temperature increases from 200 to 250 °C. The dielectric constant and flat band shift (ΔV_{fb}) depend on the magnitude of the applied bias voltage in the case of the films cured at 100 and 200 °C, implying the existence of a kind of electric field induced curing effect. We think that this is related to the presence of the free Si–OH and amine groups. Since this is not the main topic that we want to discuss in this article, comprehensive studies of this issue will be reported later. In the case of the film cured at 250 °C, robust C–V curves

with little changes according to the gate bias conditions are shown with a significant negative ΔV_{fb} and clockwise C–V hysteresis. This robustness implies the complete formation of rigid network structures without any Si–OH and amine groups. The negative ΔV_{fb} indicates the accumulation of positive charges in the dielectric film.^{19,20}

The most striking results are obtained in the case of the film cured at 300 °C, namely a distinct large C–V hysteresis. This is in part inherited from that of the sample cured at 250 °C, but has a much different character. The width of the C–V hysteresis is as much as 18 V in the low voltage sweep mode ($-10 \text{ V} \rightarrow 10 \text{ V} \rightarrow -10 \text{ V}$) and 20 V in the high voltage sweep mode ($-30 \text{ V} \rightarrow 30 \text{ V} \rightarrow -30 \text{ V}$). The capacitance values in the accumulation region in the negative gate voltage range are not significantly different in the two sweep modes. The most striking fact is that the C–V curve of the sample cured at 300 °C is “symmetric clockwise” (showing both a positive ΔV_{fb} in the positive sweep direction and a negative ΔV_{fb} in the negative sweep direction).

There are four main mechanisms causing the C–V hysteresis, viz., the (1) mobile ion, (2) carrier injection, (3) ferroelectric-like, and (4) interface bound charge models.²¹ In the mobile ion model, the presence of mobile ions inside the dielectric films leads to clockwise C–V hysteresis, but no V_{fb} shift in the positive sweep direction. This is inconsistent with the above results of clockwise C–V hysteresis, showing a huge positive V_{fb} shift. In the carrier injection model, the electrons or holes from the silicon, according to the polarity of the bias voltage, cause a counterclockwise C–V hysteresis. This is also inconsistent with the above results of clockwise C–V hysteresis. On the other hand, in the ferroelectric-like model, owing to the field induced by the permanent dipoles, a clockwise C–V hysteresis is observed, which is similar to the effect of mobile ions. In

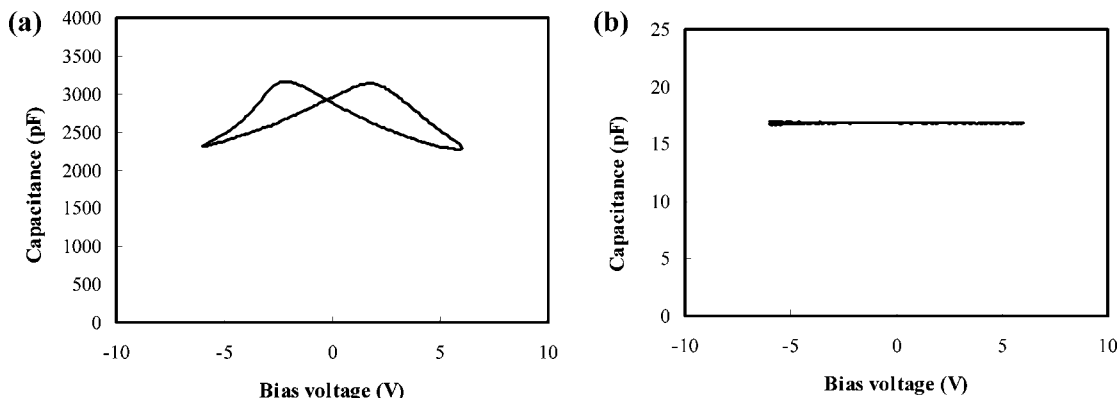


Figure 5. (a) Typical butterfly characteristics obtained for the known ferroelectric PZT thin film, indicating that our C–V measurements in the MIM device can act as an efficient methodology to check whether a dielectric thin film is ferroelectric. (b) C–V graph in the MIM device of the thin film cured at 300 °C. The absence of butterfly characteristics indicates that the ferroelectric-like mechanism is not applicable.

addition, because the dipoles appear to have equal charges whether the applied voltage is positive or negative, a symmetric hysteresis of the same magnitude is observed in the case of a positive and negative ΔV_{fb} . This is consistent with the above C–V results. On the other hand, in the interface bound charge model, it is hypothesized that there exist many bound charges at the insulator/Si interface with adjacent defect sites. At a negative gate bias voltage, electrons go through the barrier from the gate metal and fill up the defect sites in the insulator, creating a strong field which polarizes the interface bound charges. At a positive gate bias voltage, the interface bound charges are polarized in the reverse way. In the C–V measurements, the accumulation state of the silicon substrate is affected by the polarization of the interface bound charges, resulting in symmetric clockwise hysteresis. Therefore, we can provisionally conclude that the symmetric clockwise C–V hysteresis in the samples cured at 300 °C is explained by the ferroelectric-like or interface bound charge model.

We verified the feasibility of the ferroelectric-like model by conducting C–V measurements in the metal–insulator–metal (MIM) device made from the thin film cured at 300 °C. If a thin film were ferroelectric, the so-called “butterfly” characteristics would be observed.^{22–24} In order to verify this premise in our experimental conditions, a PZT thin film, which is one of the most typical ferroelectrics, was tested in the C–V measurement in our MIM device.²⁵ The typical butterfly characteristics were obtained for the known ferroelectric PZT thin film, as shown in Figure 5a, indicating that our C–V measurements in the MIM device can act as an efficient methodology to check whether a dielectric thin film is ferroelectric. However, as shown in Figure 5b, no butterfly characteristics were observed for the silsesquioxane thin film cured at 300 °C, but rather a flat C–V curve which is typical of dielectrics in the MIM device. This means that the ferroelectric-like model can be discarded for the thin film cured at 300 °C. Therefore, we can draw the provisional conclusion that only the interface bound charge model is likely to be applicable to our thin films. However, it is unexpected the capacitance value of 17 pF in the MIM device is lower than that of 23 pF in the MIS device. This is possibly due to the different substrates (platinum electrode vs silicon wafer).

The interface bound charge model in which the electrons passing through the barrier fill up the defect sites in the insulator is based on the existence of a significant amount of defect sites trapping charges in the thin film cured at 300 °C, which will be discussed in the remaining part of this paper. Before beginning an in-depth discussion on this topic, there remain two concerns

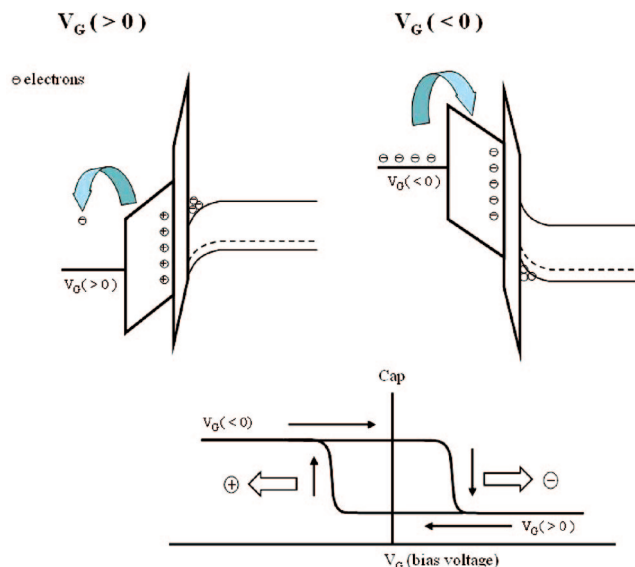


Figure 6. Modified carrier injection model explaining the distinct clockwise C–V hysteresis for the film cured at 300 °C.

to be addressed. The first point in question is what the barrier between the dielectric and silicon substrate originated from, because the curing temperature of 300 °C is not likely to be high enough to give rise to an interfacial layer acting as a high energy barrier for carriers between the dielectric layer and silicon substrate. This is explained by considering that there exists a native silicon oxide with a thickness of 19 Å on the silicon wafer. The second point is whether the interfacial polarization, whose direction is reversibly changed with changing polarity of the applied electric field, really exists in our aminopropyl-silsesquioxane system. The answer to this question is certainly “no”, because there are no special molecular structures providing significant interfacial polarization. Therefore, to explain these experimental results, we tentatively propose a *modified carrier injection model* having charge trap sites within the band gap of the dielectric thin films and a very thin energy barrier of 19 Å between the dielectric film and the silicon substrate, as shown in Figure 6, which can generate the clockwise C–V hysteresis in a similar way to the interface bound charge model. In order to verify the hypothesis that the native silicon oxide of 19 Å acts as the energy barrier, C–V hysteresis measurements with varying thickness of the silicon oxide are needed, which will be reported later.

Now, it is time to discuss what kind of defect sites or charge trap sites exist in the bulk of the film, to support the modified

carrier injection model. To explain the positive flat band shift (ΔV_{fb}) in the sweep in the forward direction, there must be defect sites that can trap electrons to form negatively charged sites. In the first-principles theoretical calculations for Si oxynitride,²⁶ the electron traps were attributed to twofold N atoms at the O sites plus an oxygen vacancy. Thus, we assume the $N(Si\equiv)_2$ structure referred to as $N(2)_O$. We conclude that the $N(Si\equiv)_2$ structure proposed in Figure 2d is the local bonding structure of the electron trap sites in the sample cured at 300 °C.

Similarly, to explain the negative flat band shift (ΔV_{fb}) in the sweep in the reverse direction, there must be defect sites that can trap holes to form positively charged sites. As regards these hole trap sites, we can consider the E' centers, which are regarded as positively charged O vacancies.^{26–28} The E' center has been reported in various silicon-related dielectrics such as SiO_2 and $SiON$.²⁸ From the molecular structure point of view, the E' center is a Si dangling bond with no electrons. What is the significance of the fact that the negative ΔV_{fb} values in the samples cured at 250 and 300 °C are greater than those in the samples cured at 100 and 200 °C? This is easily understood by remembering that part of structure VI proposed earlier in our discussion can form a kind of defect structure such as $\{ \equiv Si-O^+ + \cdot Si \equiv \}$, owing to the tensile stress accumulated during the curing process.

In summary, we initially intended to develop aminopropyl-silsesquioxane films for use as a gate insulator of OTFTs. The dielectric properties of the films such as the dielectric constant and dissipation factor are regarded as being suitable for such applications. However, the existence of charge trap sites causing a distinct clockwise C–V hysteresis is not likely to be appropriate. To clarify completely their applicability for gate insulators, a leakage current test for the aminopropyl-silsesquioxane thin films needs to be conducted, and it is also necessary to check what effects the C–V hysteresis has on the electrical stabilities in actual OTFT devices. In addition, the fine-tuning of the synthetic conditions of the resins is also crucial to enhance the electrical stability. On the other hand, the possibility of Si–N bonds being formed at 250 °C from the aminopropyl-silsesquioxane structure is very interesting, since it introduces new chemistry to the cross-linking of silsesquioxane structures for the purpose of implementing dielectric thin films. To confirm this, in addition to the FT-IR results summarized in this article, further studies using more sophisticated spectroscopic techniques are planned by our research group.

Conclusions

We synthesized aminopropyl-silsesquioxane thin films using the sol–gel polymerization reaction and characterized their electrical properties in order to assess their suitability for use as low temperature and solution-processable gate insulator for OTFTs.

The dielectric properties of these films, such as the dielectric constant and dissipation factor, in the curing temperature range 250–300 °C are likely to be regarded as promising for gate insulator applications, but the distinct clockwise hysteresis in the capacitance–voltage (C–V) measurements for the film cured at 300 °C is not desirable for the gate applications. The significant trapping of negative charges is ascribed to the formation of defect structures, such as $N(Si\equiv)_2$ with O vacancies during the curing process, whereas most of the nitrogen atoms

are likely to exist in structure networks containing $N(Si\equiv)_3$ groups without charge trapping.

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