Density Functional Theory Calculation of ^{29}Si NMR Chemical Shifts of Organosiloxanes

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Density functional theory at the B3LYP/6-311++G(d,p) level is applied to calculate the ^{29}Si NMR chemical shifts of a variety of organosiloxane moieties including monomers or precursors for polymerization and representative segments of organosiloxane polymers or thin films. The calculated shifts of two linear dimethylsiloxane compounds, hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4), compare well with their known values, having an average error of 3.4 ppm. The same method is applied to structures believed to occur in organosilicate glass thin films deposited using hot-filament chemical vapor deposition (HFCVD) from D3 and D4. The chemical shift at −15 ppm is identified as a cross-linking Si−Si bond between two strained D groups and has not previously been reported. Retention of the strained ringed structure in HFCVD films deposited from D3 is confirmed. The rings are bonded to the matrix through either Si−O or Si−Si bonds, with the latter only becoming prevalent when higher filament temperatures are employed. The strained ring structure is also observed in films deposited from a precursor with a larger unstrained ring structure, D4. These observations suggest that the known gas-phase conversion pathways of D4 to D3 and dimethylsilanone as well as the methyl abstraction reaction from D3 operate in the HFCVD reaction chemistry.

1. Introduction

Cyclic siloxanes have long been used in the synthesis of a variety of siloxane polymers.[1−6] Recently, methylated cyclic siloxanes have gained a great deal of importance as precursors for making low dielectric constant organosilicate glass (OSG) thin films via chemical vapor deposition (CVD).[7−13] Understanding the structure of these films is critical to understanding how to improve physical properties such as the thermal stability, modulus, hardness, or dielectric constant.

Structural characterization of these OSG films via ^{29}Si nuclear magnetic resonance (NMR) provides detailed resolution of the chemical bonding structure.[11,13−17] Characterizing the intricate film structure of materials created using CVD is often difficult because of the complex nature of the CVD process. As opposed to the ordered liquid-phase chemistry capable of producing nearly flawless linear polymers, plasma-enhanced CVD has incredibly complex chemistry as a result of the destructive plasma excitation of precursor gases. Even the more controllable chemistries and methods of excitation can create a material containing a never before reported bonding environment. Because there is a paucity of good model compounds for such new and complex bonding environments, many times the NMR spectra of CVD thin films contain unknown or unreferenced ^{29}Si chemical shifts.

Oftentimes, speculation based on incomplete evidence is the only means to explain the unidentified NMR peak. With the advancement of ab initio quantum mechanics and density functional theory (DFT) computing methods as well as the rapid increase in computing power, this speculation can often be tested.[18,19] Chemical shifts predicted using DFT calculations have shown good agreement with experiment.[20−24] These methods have been tested for calculating the ^{29}Si NMR chemical shifts of silanes,[21] silane derivatives,[22] silane and silanol
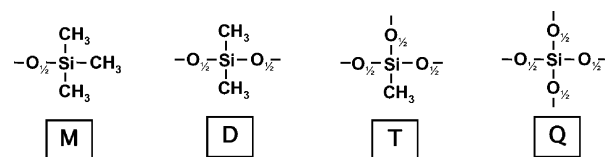

Figure 1. Nonbranching groups, M (+6 ppm) and D (−22 ppm), and branching groups, T (−68 ppm) and Q (−105 ppm), commonly found in OSG thin films with ^{29}Si chemical shifts given in parentheses.

impurities in silica clusters,[24] and SiO_2 polymorphs.[23] Additionally, DFT methods have been used to predict polymer chemical shifts using an oligomeric approach.[20]

Previous work by Gleason et al. presents the results of a hot-wire or hot-filament CVD process using hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4) to create low dielectric constant polymeric OSG thin films.[11] Hot-filament (HF) CVD utilizes a resistively heated wire, or filament, to provide the thermal energy required to excite the precursor gases which react to deposit a film on a cooled silicon substrate.[7,11,25−27] Even utilizing HFCVD for finer control over the chemistry in the deposition process, OSGs often contain complex bonding networks that do not have good model compounds for NMR reference.

There are four common bonding environments in OSG thin films.[28] Figure 1 presents the four groups resulting from fully methylated OSG precursors. Precursors with different groups bonded to the silicon will have analogous structures. An M unit is a chain terminator containing three methyl groups (monooxygen). A D unit is a linear unit bonded to two methyl groups and two oxygen atoms (dioxygen). The T unit is a branching group forming network bonds and has one methyl group and three oxygen atoms (trioxygen). Finally, a Q group is silicon bonded to four oxygen atoms (tetraoxygen) as in pure silicon dioxide. The NMR assignments are as follows: M (+6 ppm), D (−22 ppm), T (−68 ppm), and Q (−105 ppm), relative to the peak for tetramethylsiliane (TMS).[14,29] In the case where

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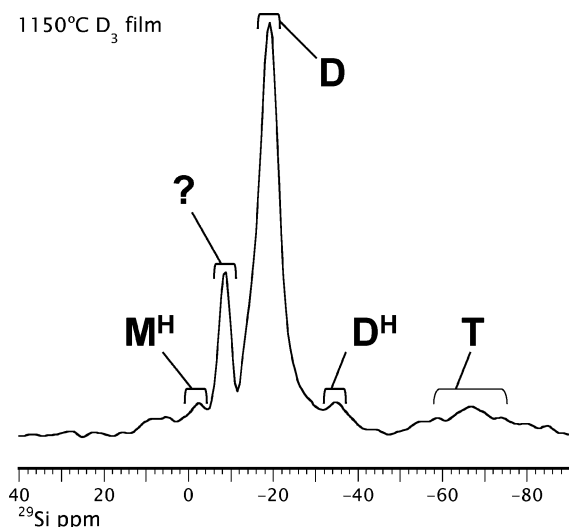
Figure 2. Labeled ^{29}Si NMR spectra of an HFCVD film from D3 with a filament temperature of 1150 °C.

one of the methyl groups of an M or D group is replaced by a hydrogen atom, the groups are referred to as M^H (−6 ppm) and D^H (−34 ppm), respectively.[14,29]

As shown in Figure 2, the ^{29}Si NMR spectra of films deposited via HFCVD from D3 display a predominance of D units, with significantly lower incorporation of M^H, D^H, and T units. Additionally, the second most intense peak in Figure 2 appears at a chemical shift of −9 ppm, which was previously unreported in the literature of OSG thin films.[11]

In this paper, the accuracy of various ab initio quantum mechanics methods for predicting NMR chemical shifts will be evaluated for known shifts of OSG film bonding environments. Additionally, model compounds representing complex portions of the OSG film matrix, some containing more than 60 atoms and over 270 electrons, will be used to aid the assignments of unknown bonding environments evident in ^{29}Si NMR spectra of OSG thin films. Finally, the insights provided by the new assignments concerning OSG film structure and deposition chemistry will be discussed.

2. Methodology and Experiments

Structures of interest were built using GAUSSVIEW, and all calculations were performed using the program GAUSSI-AN98[30] on a variety of computers with a minimum of dual 1.0 GHz Intel Pentium III processors and 512 MB of RAM. Geometries were initially optimized using the Hartree−Fock (HF) method with a 6-31G(d) basis set and further refined using the density functional theory B3LYP method with the expanded 6-311++G(d,p) basis set. The B3LYP method[31] utilizes a three-hybrid functional combining the HF and Slater exchange, the 1988 Becke density gradient correction to exchange,[32] the LYP functional of Lee, Yang, and Parr[31,33] for both local and nonlocal correlation, and the 1980 VWN functional III of Vosko, Wilk, and Nusair for local correlation.[34] The B3LYP hybrid functional has proven to provide accurate geometries while not as computationally expensive as higher order methods such as Møller−Plesset perturbation theory and the complete basis set theory.[35,36]

NMR shielding tensors were then calculated for the optimized geometries at the B3LYP/6-311++G(d,p) level. Both sets of polarization and diffuse functions were utilized to increase the accuracy of the electron density of the structures to properly simulate the shielding of the molecules. The B3LYP method

was found to provide excellent agreement with experimental results for silanes.[21] GAUSSIAN98 provides four methods for computing NMR shielding tensors, the continuous set of gauge transformations (CSGT) method,[37−39] the gauge-independent atomic orbital (GIAO) method,[40−44] the individual gauges for atoms in molecules (IGAIM) method,[37,38] and the single-gauge origin method, which is a known bad method for large systems.[30] The NMR shielding tensors were calculated using all available methods.

Of interest in this work are the ^{29}Si NMR shielding constants of a variety of siloxane molecules and structures including the standard reference compound for ^{29}Si NMR, TMS. The isotropic shielding constants for each compound of interest are calculated using DFT methods previously described and compared to the isotropic shielding constant for the reference TMS calculated at the same level. The chemical shift on the relative δ scale is calculated as follows, where δ is the chemical shift (ppm) and σ_{iso}^{TMS} and σ_{iso}^{*} represent the isotropic shielding constants of the reference (TMS) and atom of interest (*), respectively, which sets the chemical shift of TMS equal to zero:

$$\sigma_{iso}^{TMS} - \sigma_{iso}^{*} = \delta*$$

This sets the chemical shift of TMS equal to zero. Molecules simulated in addition to the reference TMS include the cyclic siloxanes tetramethylcyclodisiloxane (D2), D3, and D4. Additionally, structures containing moieties believed to exist in OSG thin films are also modeled and are shown in Figure 3. Two approximations of the linear D group found in poly-(dimethylsiloxane) (PDMS) are simulated, one consisting of a D group capped by SiH$_3$ groups (group A) and the other consisting of two linear D groups with M^H end groups (group B). Some unique OSG network forming structures were simulated as well including two methyl-abstracted D3 rings bonded together via a Si−Si bond (group C), a methyl-abstracted D3 bonded to a linear chain of three D units via a Si−Si bond (group D), a methyl-abstracted D3 bonded pendant to a linear chain of three D units via a Si−O bond (group E), and a methyl-abstracted D3 bonded terminal to a linear chain of two D units via a Si−O bond (group F). Methyl-abstracted D3 rings which are incorporated into a larger structure through Si−O or Si−Si bonds will be referred to as i-D3 to differentiate the free D3 ring from the structure incorporated into the film.

3. Results and Discussion

Computed chemical shifts relative to the peak for TMS calculated via the GIAO, IGAIM, and CSGT methods are reported in Table 1 along with available literature values. The average error for each method is reported and compares favorably with those from the work of others. Reported errors for DFT calculations are typically on the order of 2−12 ppm,[21,22,24] with errors larger than 25 ppm for silicon at the center of a single shell and as small as ±1 ppm for a silicon at the center of the large three-shell approach of Xue et al. for silicon polymorphs.[23]

All four compounds in Table 1 have reported values of experimentally determined ^{29}Si NMR shifts. The first two are cyclic molecules comprised only of D units. The last two are linear structures, group A (Figure 3a) and group B (Figure 3b). The chemical shifts calculated by all three methods agree well with literature data for the strained D moiety in D3. The six-membered D3 ring is a planar ring that does not allow for the typical 160 ± 15° ∠OSiO bond angle creating 2.5 kcal/mol of ring strain.[45,46] The calculated ∠OSiO bond angle is only 134.1°
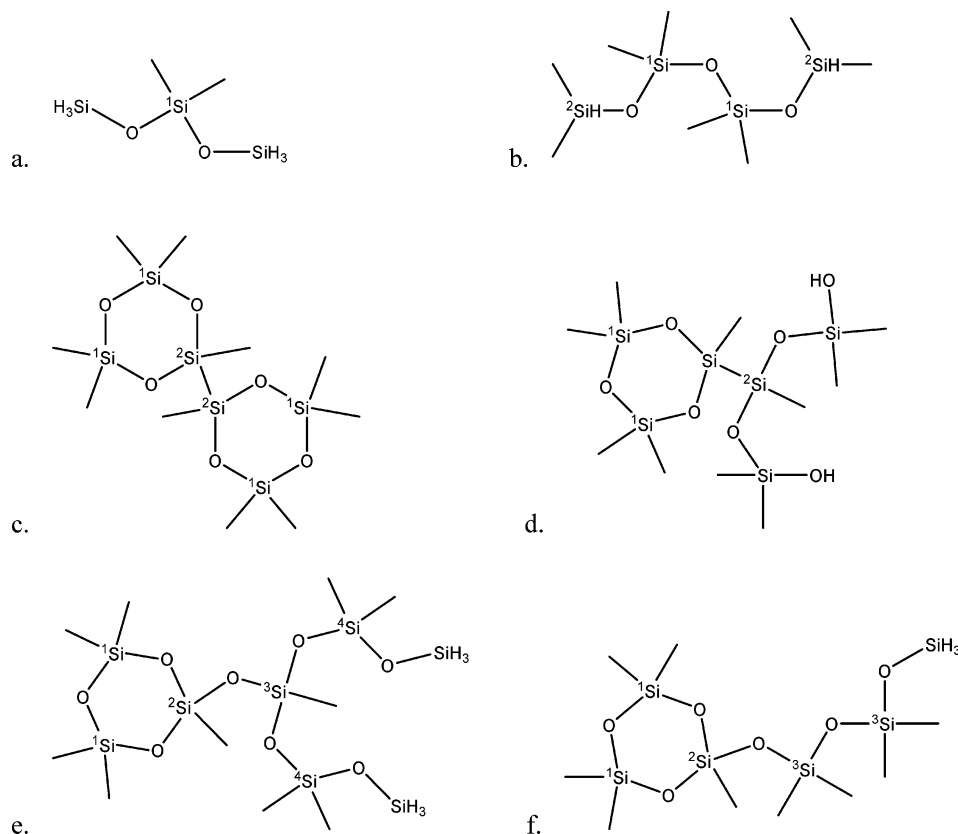
Figure 3. OSG groups simulated: (a) SiH$_3$-capped D, (b) D groups with M^H end groups, (c) two i-D3 rings bonded via Si−Si, (d) i-D3 pendant to linear chain of three D units via Si−Si, (e) i-D3 pendant to linear chain of three D units via Si−O, (f) i-D3 terminal to linear chain of two D units via Si−O (i-D3 ≡ methyl-abstracted D3 incorporated into the film structure).

TABLE 1: Summary of Calculated ^{29}Si NMR Chemical Shifts of Known Moieties Using Various Methods at the B3LYP/6-311++G(d,p) Level [a]

group	structure	lit. δ, ppm	refs	GIAO δ, ppm	IGAIM δ, ppm	CSGT δ, ppm
D3	(SiO)$_2$Si*(CH$_3$)$_2$ [D]	−8.9, −9.9	14, 29	−4.8	−8.8	−8.8
D4	(SiO)$_2$Si*(CH$_3$)$_2$ [D]	−19.5, −20.2	14, 29	−24.0	−27.4	−27.4
group A (chain)	(SiO)$_2$Si^1(CH$_3$)$_2$ [D]	−22.4, −23.5	14, 29	−17.7	−21.7	−21.7
group B (chain)	(SiO)$_2$Si^1(CH$_3$)$_2$ [D]	−22.4, −23.5	14, 29	−23.9	−27.3	−27.3
	(CH$_3$)$_2$(H)Si^2(OSi) [M^H]	−6.5	14, 29	−7.3	−10.5	−10.5
				$|\Delta|^a_{av} = 3.14$	$|\Delta|^b_{av} = 3.55$	$|\Delta|^c_{av} = 3.55$

[a] TMS σ_{iso}: GIAO, 339.2 ppm; IGAIM, 338.0 ppm; CSGT, 338.0 ppm. $|\Delta|^i_{av} \equiv$ average difference between the DFT-calculated shift and average literature values for (a) GIAO, (b) IGAIM, and (c) CSGT methods.

with a ∠SiOSi bond angle of only 105.9° as opposed to the typical tetrahedral 109.5° which deshields the silicon and causes the shift downfield from an unstrained D group. By comparison, D4 has a ring strain of only 0.24 kcal/mol, and rings containing eight or more siloxane units are thought to have no ring strain.[45,46] Bond angles for D4 were calculated to be 160.55° and 109.46° for the ∠OSiO and ∠SiOSi bond angles, respectively. The difference in chemical shift of the D unit in D3 versus D4 is a result of this large difference in ring strain and the ∠SiOSi and ∠OSiO bond angles. The increased strain in D3 reduces shielding and pushes the experimentally observed chemical shift of the D unit in D3 downfield. The DFT calculations also predict this effect; however, the absolute magnitude of the agreement between calculation and experiment for D4 is not as good as in the case of the D3 molecule. The D3 molecule is planar, and the silicon atoms are surrounded by a cloud of methyl groups, making interactions of the silicon atoms with other molecules difficult. However, D4 is a larger and slightly puckered ring, allowing for interactions of the silicon atoms with other molecules. These calculations were performed on single molecules, while the reference chemical shifts were obtained by solution NMR. The difference between the calculated and experimental chemical shifts for D4 can be attributed to molecular interactions that are not accounted for in the simulation. This error could likely be reduced by taking an approach similar to the three-shell approach of Xue et al.,[23] but not without a very large computational cost.

The difference between the unstrained D group in group A and group B is a result of the conformation of the optimized geometry. The short unstrained D group represented in group A allows the oxygen to remain in the gauche position, placing a methyl group in the trans position, while the lowest energy confirmation for group B places an oxygen atom in the trans position (as in PDMS[47]), providing greater shielding (corresponding to the shift upfield).[48] The calculated shifts for both linear D groups and the M^H moiety agree with the literature values. The relative agreement of the IGAIM and CSGT methods and GIAO method with literature values for known molecules indicates the validity of DFT as a predictive methodology for ^{29}Si NMR shifts for organosiloxanes.

TABLE 2: Summary of Calculated ^{29}Si NMR Chemical Shifts of Unknown Moieties Using Various Methods at the B3LYP/6-311++G(d,p) Level[a]

group	structure	GIAO δ, ppm	IGAIM δ, ppm	CSGT δ, ppm
D2	$(SiO)_2Si^*(CH_3)_2$ [D]	34.3	32.2	32.2
group C (two i-D3 rings)	$(SiO)_2Si^1(CH_3)_2$ [D in strained ring]	−4.2	−8.5	−8.5
	$CH_3(SiO_2)Si^2Si^2(SiO_2)CH_3$	−12.4	−15.9	−15.9
group D (i-D3 pendant to linear chain via Si−Si)	$(SiO)_2Si^1(CH_3)_2$ [D in strained ring]	−2.0	−5.8	−5.8
	(Si of strained ring)$Si^2(SiO_2)CH_3$	−25.0	−29.6	−29.6
group E (i-D3 pendant to linear chain via T)	$(SiO)_2Si^1(CH_3)_2$ [D in strained ring]	−3.8	−7.6	−7.6
	$(SiO)_3Si^2(CH_3)$ [T in strained ring]	−63.5	−64.5	−64.5
	$(SiO)_3Si^3(CH_3)$ [T in chain]	−75.0	−76.0	−76.0
	$(SiO)_2Si^4(CH_3)_2$ [D in chain]	−17.5	−20.7	−20.7
group F (i-D3 termination of linear chain via T)	$(SiO)_2Si^1(CH_3)_2$ [D in strained ring]	−4.7	−7.9	−7.9
	$(SiO)_3Si^2(CH_3)$ [T in strained ring]	−63.7	−65.1	−65.1
	$(SiO)_2Si^3(CH_3)_2$ [D in chain]	−21.6	−24.9	−24.9

[a] TMS σ_{iso}: GIAO, 339.2 ppm; IGAIM, 338.0 ppm; CSGT, 338.0 ppm.

Reported in Table 2 are the chemical shifts of five moieties which are not represented by precise model compounds in the experimental ^{29}Si NMR literature. The first structure is a cyclic dimer of D units, while the structures of the final four molecules are shown in Figure 3c−f, and will be referred to as groups C, D, E, and F, respectively. The later structures represent different means for incorporation of a six-memebered D3-like ring, i-D3, into the film structure through either Si−Si or Si−O bonds. Due to the molecular instability of D2, a measured chemical shift for the very strained D moiety in D2 has not been reported in the literature. The calculated shift of approximately +32 ppm is consistent with the trend of decreased shielding with increased ring strain and decreased ∠OSiO (88.7° calcd) and ∠SiOSi (91.3° calcd) bond angles as evident when the shift of D3 is compared to that of D4. Group C revealed a new shift for a Si−Si bond between two strained D groups occurring at approximately −15 ppm, while the shift for the strained D group in the six-membered rings remains constant. If the i-D3 ring is bonded to an unstrained silicon via a Si−Si bond as in group D, the chemical shift of the unstrained silicon is approximately −30 ppm. The shift upfield for this Si−Si bond as compared to the Si−Si bond in group C is expected due to less strain on the silicon. The calculated shift of strained D in group D of approximately −6 ppm is likely a result of interactions with the hydroxyl end groups of the linear PDMS chain. The calculated shifts for groups E and F agree very well with the shifts expected from the literature. The downfield shift of the strained D group in groups E and F as compared to D3 is due to the oxygen of the T group, which further strains the ring opposite the T group, reducing the ∠OSiO bond angles an additional 0.3−4°. The calculated chemical shifts for the linear D moieties of both groups E and F agree well with the literature value for linear D groups reported in Table 1. The chemical shifts of the T groups in groups E and F agree well with the observed spectra presented in Figure 2. The shifts of the T groups within a strained ring agree well with the reported literature value of −65 ppm for a simple T group surrounded by M groups, $CH_3Si^*[OSi(CH_3)_3]_3$, which is shifted slightly downfield compared to a generic T group, $CH_3Si(O−)_3$, with a reported shift of −68 ppm.[29] These strained T groups are shifted approximately 10 ppm downfield from the calculated shift of the T group bonded to unstrained D groups in group E. This shift is of the same magnitude as the shift between strained and unstrained D groups and is a result of the strain on the silicon atom and the resulting decreased ∠OSiO bond angles as two of the three oxygen atoms in the strained T groups are incorporated into an i-D3 ring.

All strained D moieties of six-membered rings fall in the range of −2.0 to −8.8 ppm, while linear D moieties fall in the range between −17.5 and −27.3 ppm for the compounds simulated in Tables 1 and 2. The chemical shift for Si−Si bonds associated with strained rings appears at −15 ppm. These assignments will be applied to evaluate previously published NMR spectra of HFCVD OSG thin films.

A series of films deposited via hot-filament CVD from D3 and D4 precursors were examined in previous work.[11] High-resolution solid-state NMR spectra were acquired on a home-built NMR spectrometer[49] equipped with a 6.338 T Oxford superconducting magnet and a 3.2 mm Chemagnetics probe with spinning capabilities up to 25 kHz. Magic angle spinning and cross-polarization (CP) from the proton spin bath were used to resolve isotropic chemical shifts and reduce acquisition time. A ^{1}H−^{29}Si CP time of 5 ms was chosen to maximize the overall signal intensity. Experiments confirmed that the contact time between the silicon and proton spin baths was sufficient to provide uniform ^{29}Si polarization. Indeed, a direct comparison of NMR spectra acquired with direct polarization and cross-polarization confirmed that CP spectra were quantitative. All NMR spectra were referenced to TMS and are plotted in parts per million. The ^{29}Si NMR spectra of OSG of these films contain a number of shifts previously assigned through reference to the literature. The peaks at −6, −20, and −67 ppm were assigned to the shifts corresponding to M^H, D, and T groups, respectively. Additionally, the spectra of these films contained a shift at −9 ppm which could not be definitively assigned. The calculated shifts confirm the previous assignments accounting for the M^H group at −6 ppm (group B), the unstrained D at −20 ppm (groups A, B, E, and F), and the T group at −67 ppm (groups E and F) while suggesting that the shift at −9 ppm corresponds to a strained D group (groups C−F) resulting from the i-D3 rings contained in the film structure. For films deposited from D3, this is possible through a methyl abstraction reaction of the D3 precursor, creating a radical able to bond to an existing radical site on the film. For films deposited from D4, D3 must first be produced via the intramolecular conversion of D4 to dimethylsilanone and D3, which can undergo a subsequent methyl abstraction reaction. The intramolecular reaction has an activation energy of 300.9 ± 6.1 kcal/mol, which is less than the 383 ± 39 kcal/mol required for methyl abstraction from a D3 molecule.[50,51] Bands corresponding to ring deformation for both D3 and D4 can be observed and differentiated using Raman spectroscopy.[52] Raman spectra of HFCVD OSG thin films from both D3 and D4 contain the clear signature of a six-membered i-D3 ring, providing further evidence of ring incorporation.[11]
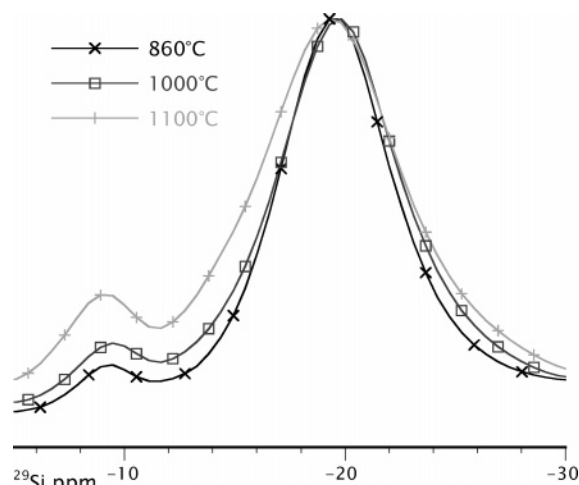
Figure 4. ^{29}Si NMR of HFCVD films from D3 with filament temperatures of 860, 1000, and 1100 °C.

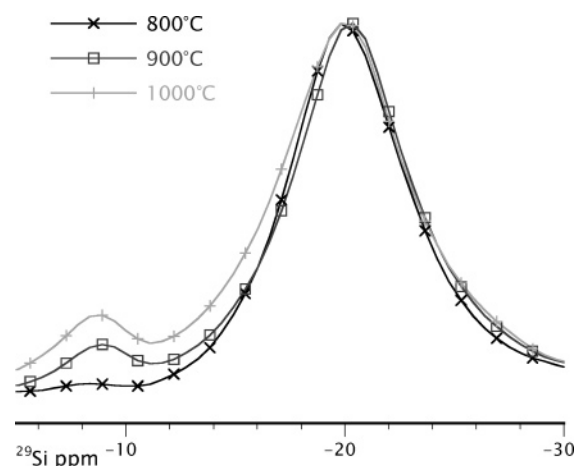**Figure 5.** ^{29}Si NMR of HFCVD films from D4 with filament temperatures of 800, 900, and 1000 °C.

The degree of ring incorporation increases with increasing filament temperature for films from each series as shown in the ^{29}Si NMR spectra in Figures 4 and 5. The i-D3 rings can be bonded to the film via Si—Si bonds as in groups C and D or through T groups as in groups E and F.

Closer inspection of the ^{29}Si NMR spectra of these films shown in Figures 4 and 5 between −5 and −30 ppm provides insight into the bonding environment of i-D3 rings included in the film. Least-squares fitting of the spectra to resolve individual peaks can determine the contributions of each type of bonding environment. While the majority of the films show only a small degree of Si—Si bonding, the film deposited from D3 with a filament temperature of 1150 °C contains a significant amount of Si—Si bonding, indicating the presence of i-D3 rings tiled to each other through Si—Si bonds. From the calculated spectra of group C, we expect a peak at −8 ppm for the strained D and −15 ppm for the Si—Si bond in addition to the backbone of linear D present in the film and occurring at −21 ppm as calculated in group B. Figure 6 shows the fit spectra. The peaks are centered at −8.5, −14.5, and −19.1 ppm corresponding to the strained D in i-D3, cross-linking of strained D groups via a Si—Si bond, and linear D, respectively. The integrated area of the peak at −8.5 ppm must be at least 2 times as large as the peak at −14.5 ppm to correctly account for the number of bonds. The integrated area of the strained D peak is approximately 3.1 times the area of the peak corresponding to the Si—Si bond,
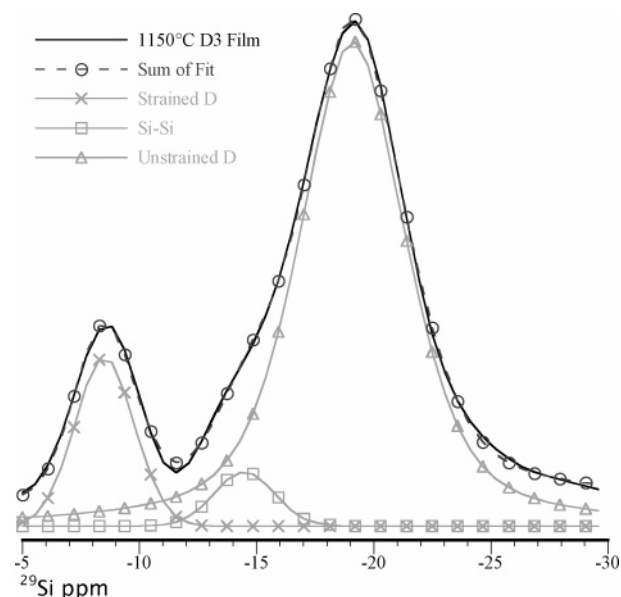

Figure 6. ^{29}Si NMR spectra of a 1150 °C D3 film fit to resolve chemical shifts at −8.5, −14.5, and −19.1 ppm.

indicating that while a large number of the i-D3 rings are bonded to the film through Si—Si bonds, there is evidence to support i-D3 incorporation through a Si—O bond in a T group either pendant or terminal to a PDMS-like chain of linear D groups as well as represented by groups E and F.

Least-squares fitting of the spectra from the remaining deposition conditions indicates an increased concentration of methyl-abstracted D3 molecules as a function of temperature. This is evidenced by the increasing presence of the strained D moiety and by the increasing presence of the strained Si—Si bond relative to that of the strained D moiety. This relative increase as a function of increasing temperature indicates that at elevated temperatures the methyl-abstracted D3 molecules can react with each other to create a structure similar to that of group C. The evidence of Si—Si bonds between strained D groups as would occur if many i-D3 rings were "tiled" together is only convincing at very high filament temperatures, >1100 °C. This coupled with the fact that there is no spectroscopic evidence of i-D3 bonded via a Si—Si bond pendant to a linear chain as in group D indicates that the majority of i-D3 rings are bonded to the structure of the film through T groups either pendant or terminal to linear chains as in groups E and F, respectively.

4. Conclusions

Using density functional theory at the B3LYP/6-311++G-(d,p) level and three methods of calculating NMR shielding tensors (GIAO, IGAIM, and CGST), the known chemical shifts of OSG compounds were calculated to within an accuracy of 0.1−7.4 ppm with an average error of approximately 3.5 ppm. This compares favorably with results of similar work which yielded errors on the order of 6−10 ppm,[22] errors of 0.2−11 ppm with a relative error of 10% on the shifting of neighbors,[24] and errors as large as 26 ppm for the one-shell approach and as small as ±1 ppm for the large three-shell approach used by Xue et al.[23] Molecules containing over 60 atoms and more than 270 electrons were successfully modeled, providing reasonable models for portions of the OSG matrix. The same methods were used to calculate the chemical shifts for previously unassigned bonding environments.

The chemical shift reported at −15 ppm and assigned to the cross-linking Si−Si bond between two strained D groups has not previously been reported in the literature to the knowledge of the authors and leads to a greater understanding of the structure of thin films deposited from cyclic siloxanes. Retention of the strained ringed structure in HFCVD films deposited from the D3 precursor is confirmed. The i-D3 rings are bonded to the matrix through either Si−O or Si−Si bonds, with the latter only becoming prevalent when higher filament temperatures are employed. The strained ring structure is also observed in films deposited from a precursor with a larger unstrained ring structure, D4. These observations suggest that the known gas-phase conversion pathways of D4 to D3 and dimethylsilanone as well as the methyl abstraction reaction from D3[11,50,51] operate in the HFCVD reaction chemistry.

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