

Carbon content of silicon oxide films deposited by room temperature plasma enhanced chemical vapor deposition of hexamethyldisiloxane and oxygen

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Hexamethyldisiloxane is used as a silicon-source gas for plasma enhanced chemical vapor deposition (PECVD) growth of silicon oxide films for passivation layers in microelectronics. In order to produce low permeability films, it is necessary to minimize the carbon content. Films were deposited by a room temperature PECVD process in a parallel plate reactor, and were characterized by infrared spectroscopy, ellipsometry, microbalance, and elastic recoil detection (ERD). The infrared-active carbon groups appear in Si-CH₃, CH_x, C=O, and SiC bands. A double band at 2343 cm⁻¹ has also been seen to track these bands. Deposition rate data shows linear behavior as a function of the Hexamethyldisiloxane (HMDSO) concentration in the reactor. The carbon within the films ranges from 36% to <1% of the amount of carbon assisted with HMDSO required to grow the films, depending upon the oxygen flow rate. By comparing the ERD composition data to the infrared spectral data, a carbon content correlation value has been found, and a detailed study of the data reveals evidence of C-C bond existence within films having the greatest total carbon content. Finally, it appears that the 2343 cm⁻¹ band corresponds to CO₂ rotational bands, in which the distribution of rotational states is evidence of hindered molecular motion.

I. INTRODUCTION

Organosilicon precursors for plasma enhanced chemical vapor deposition (PECVD) of silicon oxide have been used for some time as alternatives to silane. Their primary advantages are the ability to create conforming layers on the small surface features of integrated circuits, reduce particulate formation, and their relative ease of handling compared to silane.¹ Hexamethyldisiloxane (HMDSO) also has the added advantages of lower cost relative to silane and tetraethoxysilane (TEOS), and a higher room temperature vapor pressure (48 Torr) than TEOS (4 Torr). [HMDSO is a molecule consisting of a disiloxane (Si-O-Si) backbone with three methyl groups bound to each silicon atom.] However, organosilicon compounds add a degree of processing complexity because the carbon concentration must be minimized in the film. Plasma deposition of silicon oxide films by HMDSO has been reported with respect to the thermal activation of surface processes in film growth.^{2,3} The goal of the research presented here is to examine the films of a room temperature process, since such temperatures are required for applications in which the substrate has a very low glass transition temperature or melting point (e.g., polyethylene terephthalate, *T_g* ~70–90 °C). Plasma enhanced chemical vapor deposition provides a mechanism to initiate the chemical reactions that produce silicon oxides at such reduced substrate temperatures.

This article focuses on issues related to the film growth using room temperature plasma deposition of HMDSO and oxygen. The primary issues are how silicon precursor dilution governs film deposition and composition. Analysis of process conditions, and composition and infrared spectral data shows general trends in the behavior of the deposition system and the chemical make-up of the films. Infrared data is correlated with the total carbon content of the films so that

carbon compositional estimates of the films can be readily made. Furthermore, with these data it is possible to construct a model that estimates the relative concentration of various atom bond pairs. This information can explain the ability of a particular process to drive the chemical oxidation of the precursor material to completion. It will be shown, that while the deposition is rate-limited by the HMDSO concentration, the carbon content in the films does not obey the same behavior. Films that are similar to silica glasses deposited by other plasma processes are deposited with high dilution of HMDSO in oxygen, while the low dilution produce plasma-polymerized films containing carbon bound in chemical groups not found in the precursor.

II. EXPERIMENT

The analytical techniques for sample analysis included ellipsometry, elastic recoil detection (ERD), and infrared absorption spectroscopy. The ellipsometer used for film thickness measurements was a Gaertner L116A. The ERD measurements were performed at the University of Montreal using their tandem accelerator with 30 MeV Cl⁺⁵ ions. For more details on ERD analysis refer to papers by Groleau and Currie.^{4–6} The infrared spectral data collected between 430 and 4010 cm⁻¹, were obtained in normal-incidence transmission at 8 cm⁻¹ resolution with 32 scans, using the "micro-beam" sampling position of a Bomem MB155 FTIR spectrometer. Unity subtraction of substrate absorbances was performed in this sampling mode and applied to the spectra.

The reactor in which the films were grown was a parallel plate system where the electrode spacing was 2 cm, and the electrodes themselves were 10.1 cm diameter Al plates. The top plate was connected to the chamber ground, and the bottom plate was powered by a 250 kHz, 1.5 kW PL-2HF ENI power supply that was matched to the electrode with a 200 Ω

autotransformer. The powered electrode was insulated on all sides except its top surface by 1 cm thick Teflon insulators that extended an additional 1 cm above the surface of the powered electrode. The operating pressure of the reactor was held at 250 mTorr with a flow rate 10 sccm of HMDSO. The samples were mounted on the powered electrode and were (100) Si wafers ($\rho \geq 10 \Omega \text{ cm}$) $1 \text{ cm} \times 1.5 \text{ cm}$. The silicon oxide thin film thickness variation across the silicon substrates was less than 1%. The standard operating conditions were 200 sccm O_2 flow rate and 70 W applied rf power. To obtain the wafer density baseline for film density measurements, the wafers were diced, HF-cleaned, their dimensions measured, and then were weighed on a Cahn C-30 microbalance. Film deposition time was set to achieve approximately 1000 Å thick films. After seven days, the infrared spectrum was collected along with film thickness and film mass. The delay was to allow film relaxation so that the infrared spectra would be from conditions similar to conditions when the ERD measurements were made.

III. RESULTS

At high dilution of HMDSO in oxygen, the spectral signal approaches that of films grown by SiH_4 and oxygen in terms of the vibrational modes represented. However, as the dilution decreases, other features appear as shown in the spectra of Fig. 1. Representative spectra of plasma films deposited at several HMDSO/oxidant flow rate ratios are shown in Fig. 1. General features in the spectra are listed in the first part of Table I, features unique to films grown with low O_2 flow rates are listed in the last part of the table.⁷⁻¹¹ All spectra exhibited a sloping baseline due to optical interference at the free surface and substrate interface, which has been removed by a high order polynomial fit.

The bands at 2360 and 2337 cm^{-1} [see Fig. 1(b)], due to the asymmetric stretching vibration of the CO_2 molecule, appear in all of the spectra. For slightly oxidized films, the peak positions of PQR band contour appear normal for gaseous CO_2 ,¹² but with increasing O_2 flow rate, the lower band (P branch) grows dramatically in intensity, and shifts upward by several wavenumbers (from 2337 to 2343 cm^{-1}), and narrows to 12 cm^{-1} full width at half-maximum (FWHM).¹² Normal spectrometer purge did not remove the signal. Furthermore, the peak positions and widths are stable to 72 h vacuum pumping and aging over a period of at least two months, at room temperature. Rotational structure, if present, was not resolved at instrumental resolutions of 2 or 8 cm^{-1} . The changes in the peak envelopes are consistent with the stable confinement of CO_2 within voids of well defined size, akin to known clathrates,^{13,14} and are discussed in more detail at the end of the discussion section.

The deposition rate of thin films as a function of the relative HMDSO concentration in the reactor is presented in Fig. 2, in which the O_2 flow rate was varied between 0 and 200 sccm, and the HMDSO flow rate is 10 sccm. It shows that the deposition rate is linearly dependent upon the HMDSO concentration. Minimum deposition rate of 2000 Å/min are routinely achieved at flow rates of 200 sccm O_2 , while maximum deposition rates are 1.5–1.7 $\mu\text{m}/\text{min}$ for 10 sccm oxygen. The film density is close to that of bulk amorphous

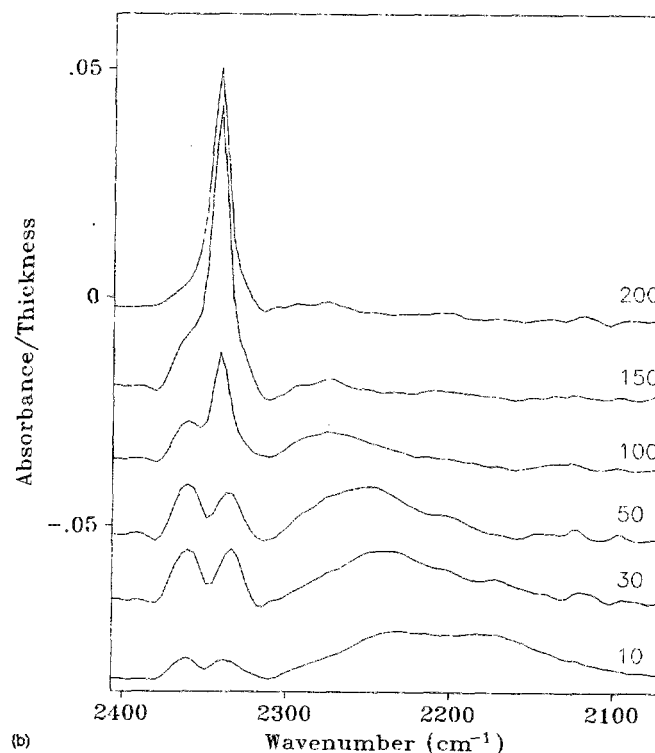
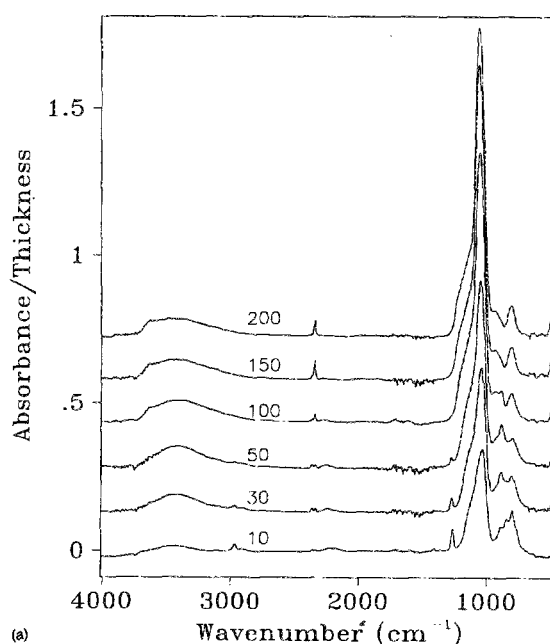


FIG. 1. (a) Infrared absorbance spectra normalized relative to the film thickness of films grown at different O_2 flow rates. O_2 flow rate in units of sccm is noted for each spectrum. Other conditions are 10 sccm HMDSO, 70 W at 250 kHz, and 250 mTorr. (b) Expansion of the 2000 to 2400 cm^{-1} region. O_2 flow rate in units of sccm is noted for each spectrum. Other conditions are 10 sccm HMDSO, 70 W at 250 kHz, and 250 mTorr.

SiO_2 , ($2.2 \text{ g}/\text{cm}^3$), at 200 sccm oxygen, but drops steadily to $1.4 \text{ g}/\text{cm}^3$ at 10 sccm oxygen. The deposition rate increases by almost a factor of 10 as the oxygen/HMDSO ratio decreases by a factor of 20.

TABLE I. Major infrared spectral features that appear in the films.

Band Position (cm ⁻¹)	Attributed source	Comments	Reference
3650, 3350	OH	Broad band	5
2360, 2335	CO ₂	Asym stretch	12
1060-1030	Si-O-Si	Asym stretch	7, 13
930-925	Si-OH	Bend	7
810-800	Si-O	Bend	7, 13
450	Si-O	Rocking	7, 13
Features that appear only at low O ₂ flow rates			
3000-2800	C-H	Stretch	8, 9
2250-2150	Si-H	Stretch	8
1275-1260	Si-CH ₃	Bend	8
885-800	Si-C ₂ H	Bend	8
1720	C=O	Stretch	13

The dilution of HMDSO by oxygen in the discharge produces changes in the composition of the film as shown through infrared spectroscopy. One of the more significant changes is the lowering of the carbon content of the films shown in Fig. 3. It shows the decrease in the film-thickness-normalized integrated area of the 1275, 1720, 2911, and 2950 cm⁻¹ bands. The plot shows a monotonic decay between the O₂ flow rate and the 1275, 2911, and 2950 cm⁻¹ bands, which are all related to C-H bonding. The 1720 cm⁻¹ (C=O) band, on the other hand, does not show a clear dependence on the O₂ flow rate, but does disappear above 100 sccm oxygen. It should be noted that the deposition rate is proportional to the 1275 and 2911 cm⁻¹ bands. This demonstrates a linear relationship between the rate at which the thin film network propagates and the incorporation rate of methyl groups within the film.

The infrared band attributed to the Si-O-Si stretch mode undergoes changes as the O₂ flow rate changes. For example, the 1060 cm⁻¹ band shifts towards lower wave numbers by as much as 30 cm⁻¹ and the lower wave number side of the band grows. In addition, the 1150 cm⁻¹ shoulder on the peak increases in height relative to the 1060 cm⁻¹ band. It also shifts down in wave number, since it appears to merge more than the 1060 cm⁻¹ band as the O₂ flow rate decreases. The

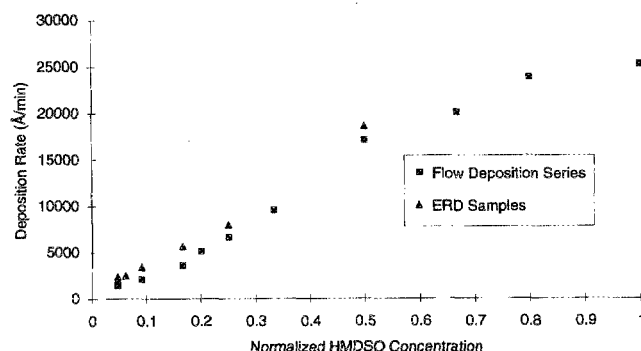


FIG. 2. Deposition rate as a function of the normalized HMDSO concentration time within the reactor. The normalized HMDSO concentration is calculated as the ratio of the HMDSO flow rate over the total flow rates for 10 sccm HMDSO, and 0-200 sccm O₂, 70 W, and 250 mTorr.

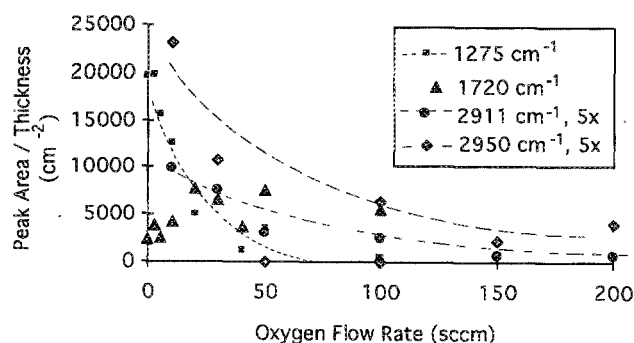


FIG. 3. Absorbance band area normalized against film thickness as a function of the O₂ flow rate for films grown with 10 sccm HMDSO; 70 W at 250 kHz, 250 mTorr, and 17 s. The lines are drawn to guide the reader.

FWHM decreases from 125 cm⁻¹ at 10 sccm to about 83 cm⁻¹ at 200 sccm. 83 cm⁻¹ is typical for silicon oxides grown by plasma processes. The FWHM of the 1060 cm⁻¹ band is a measure of the spread in the distribution of the bond angles of the Si-O-Si groups upon which the glassy network is based.¹⁵

IV. DATA ANALYSIS

For thin films, the integrated area of an infrared absorption signal normalized with respect to film thickness, for a vibrational mode related to a particular chemical feature, is proportional to the concentration of infrared absorbing groups. In the case of hydrogen atoms, since hydrogen has a single chemical bond, the infrared spectral feature can often be directly related to the concentration of that hydrogen-containing group. When examining atoms such as silicon or carbon that can exist in several configurations, it is usually difficult to obtain direct compositional relations. However, it is possible to relate carbon content to the infrared signal if it is kept in mind that such correlation is not directly proportional to the concentration of C-H groups. As will be shown below, the carbon exists in forms other than methyl groups.

The relationship of carbon content to the 1275 cm⁻¹ peak area is linear; it has a larger y intercept relative to the carbon content compared to the 2911 cm⁻¹ band. The slope of this curve is proportional to the correlation factor, the composition coefficient of carbon in silicon for the 2911 cm⁻¹ band is 2.5×10^{18} cm⁻¹. Similarly, the fit for the 1275 cm⁻¹ band is a slope of 7.8×10^{17} cm⁻¹. The slopes of these curves may be higher than correlation coefficients for OH, SiH, and NH groups in silicon thin films ($\sim 10^{15}$ - 10^{16} cm⁻¹), because ERD includes carbon bound in other chemical groups.¹⁶

Elastic recoil detection provides accurate thin film compositional data, but by using it with knowledge of processing conditions and film density, one can determine certain probabilities related to atom incorporation. The product of the atomic concentration and the deposition rate determines the flux density at which carbon is incorporated into the film. These values are a measure of the net incorporation rate of the atom, on the basis of all reactions that incorporate or remove atoms from the film. They can therefore be used to

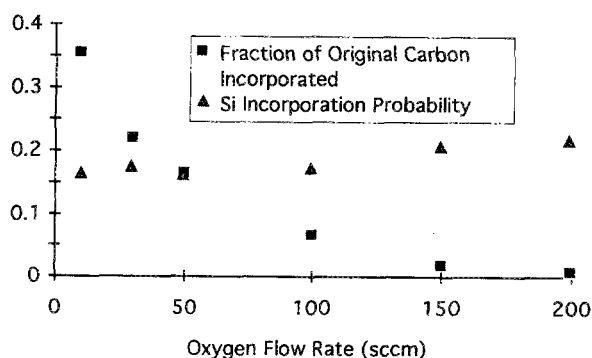


FIG. 4. Fraction of carbon contained in films relative to amount of carbon contained in HMDSO used to grow the films, and the incorporation probability of silicon atoms into the film as a function of the O_2 flow rate.

calculate various probabilities related to atom incorporation into the film. For example, it is possible to estimate the amount of carbon injected into the reactor that is incorporated into the film. The first step is to determine the incorporation flux density of carbon incorporation into the film. By calculating the ratio of the flux density of carbon being incorporated into the film to the flux density of silicon incorporation into the film, it is possible to determine how much carbon is incorporated into the film from the fraction of precursor used for film growth. The silicon can be considered a "tracer" for the source of carbon, since all of the carbon, silicon, and hydrogen in the process comes from HMDSO. The ratio of carbon to silicon in HMDSO is 3:1, so 3 times the silicon incorporation flux density is the flux density of the maximum amount of carbon that could exist in the films. The ratio is therefore the amount of carbon incorporated into the film to the amount of carbon associated with the incorporated silicon.

Figure 4 shows how much of the carbon originally contained in the HMDSO molecule is ultimately incorporated, and the probability of a Si atom being incorporated into the film. As the plot shows, at 10 sccm oxygen, about 36% of the carbon is incorporated, but that decreases to less than 1% at 200 sccm oxygen. This is a measure of the degree of oxidation of the silicon in the films. It should be remembered that since the carbon content is measured after film growth, this value includes the effects of postdeposition reactions that may remove carbon from the film, though these reaction rates are surely lower than predicted for TEOS-grown films at elevated temperatures.^{17,18} Similarly, the ratio of the flux density of silicon incorporation into the film to the impingement rate of HMDSO provides a measure of the probability of silicon atom incorporation into the film. Assuming that silicon is either converted into the solid film or vented in the exhaust gas, then this probability determines the likelihood that silicon is incorporated into the film. The partial pressure of HMDSO in the reactor provides a measure of the impingement rate of silicon atoms on the growth surface. However, the HMDSO must form molecular fragments in the plasma, and consumption paths lower the silicon concentration in the gas phase, so the incorporation probability is a

summation of all surface and bulk reaction probabilities that lead to silicon incorporation, (it is not a true sticking coefficient). The incorporation probability demonstrates an increase in the silicon-atom incorporation ratio, varying from 0.17 to 0.23, as the O_2 flow rate increases.

By using infrared absorption data of hydrogen-containing groups, in addition to atomic concentration data, it is possible to determine the existence of bond types by accounting for the fraction of each type of bond that might exist. The significance of the demonstration is that it can provide indications of bonds types that may form during the deposition process that do not exist in HMDSO and are not detectable by infrared absorption or ERD used in this study. It will be shown in the next section that C-C bonding exists in the low-oxygen-flow-rate-deposited films, through accounting of all bonds that occur in the material.

The bond accounting scheme relies on the fact that the composition of the film is known, that there is some knowledge about the probability of certain bond combinations, and that the number of dangling bonds is minuscule. Considering that the atoms contained in these films are Si, O, C, and H, there are ten unique pairings of atoms. Therefore, in order to have a unique solution, a system of equations with ten statements must exist. The equations used for these films are

- (1) & (2) H-H and O-O do not exist in these films.
- (3) to (6) The total fraction of each type of atom must be unity.
- (7) & (8) The concentration of Si-H and O-H bonds can be measured from infrared spectroscopy.
- (9) Assume that Si-Si bonding is negligible in these films.
- (10) Assume the C-O concentration is the same as the C-H concentration.

The two assumptions are required to fully define the problem, and are justified through the following arguments. Assumption 9 is made because while the Si-Si concentration is not determinable by these experiments, there is no reason not to believe that the concentration is very low. Assumption 10 is made because the CO band around 1720 cm^{-1} tends to be more infrared active than the CH(s) bands around 2911 cm^{-1} , and the area of the CO band is smaller than the CH band.¹⁹ These two assumptions help underestimate the amount of C-C bonding in the material. The smaller peak at 1720 cm^{-2} , compared to 2911 cm^{-1} , therefore implies that the C=O concentration is less than C-H concentration.

When making the actual calculation, the fraction of bonding of a particular type of atom is found by one of three methods. The first is the analysis of the infrared spectrum, which yields the concentration of a particular bonding type,¹⁶ and it is normalized with respect to the bond concentration involving the atom. The bond concentration is defined as the product of atomic concentration and the number of bonds for the particular atom. The second method is that an atom has n number of configurations, and $(n-1)$ bond type fractions are known for the particular atom; the last bond fraction is simply unity minus the sum of all of the other bond fractions. The third uses the relationship that the fraction of one type of bond relative to one of the atoms of the bond is equal to the

product of the fraction of that type of bond relative to the second atom in the bond and the ratio of the second atom bond concentration to the first atom bond concentration. By applying these statements and relations, it is possible to derive estimates of the fractions of the different bonding types in the film.

V. DISCUSSION

It has been shown that the ratio of O/Si atoms increases linearly from 1.3 at 10 sccm oxygen until a saturation ratio of about 2.1 is reached for flow rates above 100 sccm.²⁰ The ratio shows that the films are suboxide stoichiometric at flow rates below 100 sccm oxygen. However, since silicon and oxygen can also be bound to hydrogen and carbon, a ratio of 2.0 does not necessarily correspond to a stoichiometric oxide. Figure 4 shows that even at 100 sccm, about 8% of the carbon from the HMDSO is ultimately incorporated into the film, so that if significant amounts of it are bound to silicon, then the Si-bound-to-O stoichiometry is not 2:1. The organic group fraction decreases as a function of the O₂ flow rate too. The linear relation in Fig. 2 demonstrates that the deposition rate is limited by the HMDSO concentration.

The carbon incorporation is the result of a lack of removal from either the precursor before deposition, or through post-deposition reactions. For TEOS-based silicon oxide growth, it has been recognized that exposure to the plasma and thermally stimulated pyrolysis reactions may account for post-deposition carbon removal.^{13,17,18} Stout and Kushner have shown that the subsurface layer carbon content of TEOS-grown oxides may lower the surface carbon content by as much as 0.5%.¹⁷ The ERD data for films presented here have a constant carbon concentration profile for the films grown with HMDSO with a sensitivity of 0.5%, so an analogous effect is beyond the detectability limits.

Low-oxygen-flow-rate grown films contain a good deal of carbon, which may not be in forms that exist in HMDSO. For example, the deposition process must be the source of the Si-H bonding that is seen at low O₂ flow rates (see Fig. 1 the band at 2275 cm⁻¹). Another type of bonding that may exist but cannot be detected by the techniques used in this study is C-C bonding, which is not present in HMDSO. Figure 5 shows an example of the bond accounting derivation for a film grown with 10 sccm oxygen and 10 sccm HMDSO. The diagram uses bar graphs to plot the relative fraction of bond type for each type of atom in the material. This chart shows that as much as 36.6% of the hydrogen bonds are to carbon atoms, and that a significant fraction of Si-C bonds exist in the material. At lower HMDSO dilution, a series of infrared bands that might be associated with Si-C(s) is observed between 750 and 850 cm⁻¹. However, it is difficult to deconvolute the bands to say anything quantitative about Si-C bonding in the material. The presence of Si-C bonding is not surprising because in HMDSO, 25% of the carbon bonds are attached to silicon, however, the value of 47.6% shown in Fig. 5 implies that more Si-C bonding occurs during the deposition process. The assumption that Si-Si bonding is negligible tends to maximize the estimate of Si-C bonding, though it is unlikely that Si-Si bonding could account for the entire amount. After accounting for the

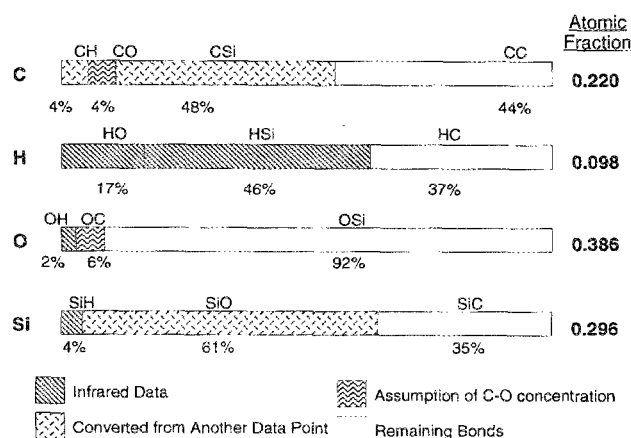


FIG. 5. Bond accounting for a film grown with 10 sccm O₂, 10 sccm HMDSO, 70 W at 250 kHz, 250 mTorr, and 17 s. The pattern of each segment of the plot indicates how each value was determined. Above each bar is the type of bonding group, below each bar are the percentage values assigned to each point, and to the right of the plot are the atomic fractions of each type of atom.

carbon bonds attached to H, O, and Si, there is a difference of 44% with a cumulative error of 27%. The cumulative error is the sum of the errors for each of the other bonding options, so some of the 44% value must be attributed to the presence of C-C bonds in the films. The conclusion is reasonable since the list of other possibilities has been exhausted. Raman spectroscopy can be employed to detect the presence of C-C bonds.

The silicon incorporation probability is the sum of all processes associated with the film growth process, in that it only examines the rate at which silicon is incorporation into the film relative to the rate at which silicon atoms within HMDSO molecules would impinge upon the surface without a discharge present. This probability data ranges from 0.23 to 200 sccm oxygen down to 0.17 at 10 sccm oxygen, a 30% decrease towards lower O₂ flow rates. At low O₂ flow rates, the partial pressure of HMDSO is a significant fraction of the total pressure and it is expected that electron excitation of HMDSO dominates. The lack of oxidizing species at lower flow rates may encourage agglomeration reactions between HMDSO fragments. At higher O₂ flow rates on the other hand, the overall plasma excitation approaches that of a pure oxygen discharge, leading to more highly oxidized HMDSO fragments. However, further experiments are needed to develop a more accurate picture of this trend.

The change in the character of the residual CO₂ band at 2343 cm⁻¹ is not expected behavior of gas phase CO₂, however, it may provide evidence about the atomic-free-volume dimensions. The observed skewing of branch intensities suggests increasingly hindered rotation of CO₂ due to confinement in progressively smaller atomic-free volumes surrounding the CO₂ molecule. Such a phenomenon for the molecule is suggested by the frequency and intensity increase of the 2343 cm⁻¹ band with oxidant dilution of the HMDSO.^{13,14} Some attempt was made to see if the band shape or intensity

could be altered by placing it in a CO₂-free environment, but no change was detected. At this time, two explanations on how the molecule is incorporated into the film are being considered. The first is that CO₂ is the product of post-deposition reactions within the film. The second, less likely explanation, is that CO₂ merely diffusing into the material from the atmosphere interacts with the film that causes the shift in the distribution of rotational states. The phenomenon does provide intriguing possibilities in studying how gas molecules interact with solid nonequilibrium microstructures.

As the O₂ flow rate decreases, the 1060 cm⁻¹ bandwidth increases [Fig. 1(a)], but does so primarily on the lower wavenumber side of the peak. It has been shown that the smaller the wave number of the band, the smaller the bond angle of the Si-O-Si group.^{15,21} The narrower bond angle groups tend to be more chemically reactive than the wider angle groups. This is caused by a repositioning of π -antibonding orbital.^{8,22} The other effect is that the atomic free volume increases in films with smaller average bond angle,²³ since the atoms of the network tend to be closer together. This is supported by the fact that the trapped CO₂ at lower flow rates shows a distribution of rotational states more like free CO₂ molecules.

VI. SUMMARY

The chemical composition of the silicon oxide films grown at different oxygen flow rates vary widely. Films grown at high O₂ flow rates exhibit infrared spectra that approach that of plasma grown silicon oxides grown at elevated temperatures (400 °C), in that the films contain very little carbon (~0.7%), yet have significant quantities of OH. The presence of C-C bonding has been indicated through an analysis of the infrared spectra for hydrogen placement in the films, and compositional data. In addition, the fraction of Si-C bonding in the plasma polymerized films appears to be greater than in HMDSO, suggesting that film networking takes place through bonding of Si and C from different HMDSO fragments. The presence of C-C bonds and Si-H bonds are evidence of the cracking which HMDSO must undergo during the deposition process. Finally, the incorporation of Si into the film increases with increasing dilution of HMDSO in oxygen, with an average value of 0.20, though at low O₂ flow rates the silicon incorporation probability appears to be largely independent of O₂ flow rate. A composition coefficient relates the total carbon content to the 2911 cm⁻¹, and the 1275 cm⁻¹ spectral features. Incorporated CO₂

in the films implies that normal rotational distribution of states in the gas phase of the linear CO₂ molecule is inhibited by some microstructural feature for films grown with higher oxygen dilution, perhaps the characteristic microscopic dimension of the film.

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