

Local bonding environments of Si-OH groups in SiO₂ deposited by remote plasma-enhanced chemical vapor deposition and incorporated by postdeposition exposure to water vapor

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We have deposited thin films of SiO₂ by remote plasma-enhanced chemical vapor deposition and have identified similar infrared (IR) spectroscopic signatures of Si-OH groups incorporated during either film growth, or the cooling down process in the deposition chamber. These films can also be hygroscopic and, on postdeposition exposure to atmospheric water vapor, they show changes in the IR spectra associated with the incorporation of additional Si-OH groups. These changes are (i) the development of a new symmetric feature, centered at about 3350 cm⁻¹, within the asymmetric O-H stretching band generated during growth and/or cooling down; (ii) the development of a new spectral feature at 925 cm⁻¹; and (iii) a shift in the Si-O bond-stretching band to higher wavenumber. We show that the first two changes in the IR spectra are due to near-neighbor Si-OH bonding groups that result from the reaction between water vapor and the Si-O-Si bonds of the SiO₂ host network. These spatially correlated Si-OH groups have different spectral features, due to relatively strong hydrogen bonding interactions, from the randomly distributed Si-OH groups that are incorporated initially during film growth and/or cooling down. The shift in the frequency of the Si-O stretching band derives from a preferential reaction of water with strained and highly reactive Si-O-Si bonding groups, i.e., those with the smallest Si-O-Si bond angles which are attacked by water vapor, resulting in the formation of near-neighbor pairs of Si-OH bonding groups.

I. INTRODUCTION

There is a great deal of interest in depositing electronic quality thin films such as SiO₂ at low temperatures, thus providing savings in the available thermal budget in many device-processing applications. Plasma-enhanced chemical vapor deposition (PECVD) techniques have proved promising in producing thin films at lower substrate temperatures than generally required for pyrolytic chemical vapor deposition processes. Direct and remote PECVD techniques have been used to produce SiO₂ films, but depending on the deposition conditions, especially at very low temperatures, 100–300 °C, these films sometimes contain relatively high concentrations of bonded hydrogen. Electronic applications, e.g., as gate dielectrics, require oxide films relatively free of bonded hydrogen, and as such PECVD films have not generally been used in applications that require a high degree of electronic quality. Most low-temperature depositions, using conventional or direct PECVD, generally result in the incorporation of between 5% and 10% bonded hydrogen in both Si-H and Si-OH groups.^{1,2} Remote PECVD oxides can also contain OH groups, but the concentration can be reduced below infrared (IR) detectable levels, ~1%, by appropriate choices of deposition process variables.³ In previous studies we have identified the deposition conditions and specific reaction pathways by which Si-H and Si-OH groups can be incorporated into remote PECVD oxide films. Si-H groups are incorporated only in hydrogenated suboxides, SiO_x:H, which can also be viewed as alloys of hydrogenated amorphous silicon, *a*-Si:H, and SiO₂, whereas Si-OH groups can

be incorporated into SiO₂ films that do not contain excess Si.^{4,5} This means that only in rare instances do Si-H and Si-OH groups appear in the same films deposited by remote PECVD.

We have previously identified two different ways in which Si-OH groups could be incorporated into remote PECVD SiO₂ films: (i) via reactions with OH containing species that occur during film deposition, or during cooling down in the deposition chamber and (ii) by postdeposition, *ex situ* exposure to atmospheric H₂O that diffuses into unprotected films and reacts to form Si-OH groups.^{6–8} We have found by analysis of IR data that the atmospheric H₂O preferentially reacts with Si-O-Si groups with smaller Si-O-Si bond angles.⁹ These strained-bonding groups are expected to be more reactive than relaxed groups with larger Si-O-Si bond angles, and in addition are more accessible to chemical attack because of localized increases in the bond-free volume associated with the strained Si-O-Si bonding groups.¹⁰ We have shown that it is possible to produce SiO₂ films by remote PECVD without IR detectable Si-OH bonding groups (<10¹⁹ cm⁻³), by using low deposition rates, substrate temperatures of about 200 °C and higher, and an O₂ content in the plasma gas <2%. When the O₂ content is in this range, it is equal to, or less than the concentration of silane molecules introduced downstream in the remote PECVD process. For this range of relative concentrations of O₂ and silane, the reaction by-product of the heterogenous surface reaction producing the oxide films is predominantly hydrogen, whereas for higher relative concentrations of O₂ the dominant by-product is water vapor.

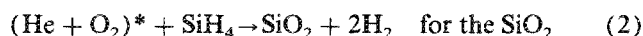
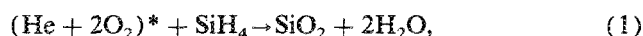
In a previous study, it was shown that there are two distinct environments in which the Si-OH groups exist in an SiO₂ host material: (i) as isolated OH groups that are incorporated via a relatively fast reaction during deposition and/or sample cooling down in the deposition chamber; and (ii) as near-neighbor pairs of Si-OH groups that are effectively hydrogen-bonded to each other, and are introduced by post-deposition *ex situ* exposure to atmospheric water vapor.⁶ More recent studies have shown that the isolated groups are introduced by postdeposition reactions that occur during the cooling down in the chamber, rather than during the deposition process itself. The rate of incorporation of Si-OH groups will depend on the particular species that is the source of the OH groups. For the near-neighbor Si-OH groups that are generated outside of the deposition chamber, water is the reactive species. For the isolated groups generated during sample cooling down in the deposition chamber, the higher rate of incorporation and the different spectral signature suggests a different mechanism, perhaps involving atomic hydrogen, a silicon molecular species containing an Si-OH group, or different types of reactive sites within the thin film structure that are more susceptible to attack by species present in the chamber ambient.

To better understand how Si-OH groups are incorporated into these films in two different ways, it is important to understand how hygroscopic SiO₂ films behave. Even though we can produce SiO₂ films that are generally not hygroscopic and do not acquire Si-OH groups during their cooling down, for this study we intentionally produced films that are hygroscopic. In this paper, we examine IR spectroscopic changes that occur upon prolonged exposure to atmospheric moisture, and relate these changes to a model of what is occurring on an atomic scale. We demonstrate how the 925 cm⁻¹ band, that appears in these films, is specifically related to only certain types of Si-OH groups. The occurrence of this band, coupled with other spectral changes, provides a basis for defining the local atomic bonding arrangements for the two types of Si-OH groups, including the extent to which strong hydrogen-bonding reactions are obtained only with specific local environments.

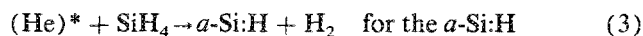
II. THIN FILM DEPOSITION BY REMOTE PECVD

All PECVD techniques involve the plasma excitation of at least some of the gaseous reactants in order to produce the chemically reactive species (e.g., radicals, ions, molecular fragments, etc.) that promote low-temperature deposition. In direct PECVD, the substrate and all of the gases in the deposition chamber are exposed to the plasma, generally generating many different simultaneous or parallel deposition reaction pathways. The large variety of deposition reaction paths in conventional and direct PECVD processes then makes it difficult to control the stoichiometry and purity of the deposited thin films. One exception to this general observation is a nonconventional direct PECVD process, the Batey-Tierney process for SiO₂, in which extremely high dilution of the process gases limits precursor formation and therefore the number of multiple reaction pathways, thus leading to formation of stoichiometric, hydrogen free, device quality thin films.¹¹

The remote PECVD process also affords a high degree of control over the thin film composition by restricting plasma excitation to a subset of the process gases and thereby reducing the formation of plasma-activated precursors and the associated multiplicity of reaction pathways. The fundamental difference between conventional direct PECVD and remote PECVD is that process reaction flow is sequential or serial, rather than parallel. Specifically in remote PECVD, a subset of process gases is plasma excited, and activated species extracted from the generation region and transported into the plasma-free deposition chamber mix with the remaining process gases. This mixture of active species and downstream injected process gases react heterogeneously to form a thin film on a heated substrate.^{12,13} For SiO₂ depositions, the Si containing gas silane, SiH₄, is always injected downstream from the plasma region. A mixture of a noble gas, usually He, and either O₂ or N₂O is plasma excited, and is the source of the oxygen atoms in the deposited thin films. By a combination of different gas injection points, flow rates, and process pressures, the silane can be prevented from backstreaming into the plasma region, thereby eliminating deposition reaction pathways that derive from the direct plasma excitation and breakup of that species. The pathways associated with silane breakup, as in direct PECVD, are generally those responsible for departures from stoichiometry in the Si/O ratio and for the incorporation of bonded hydrogen in Si-H and Si-OH environments. We have identified two specific pathways for the deposition of the SiO₂ films by remote PECVD, and one for *a*-Si:H⁴; these are



depositions, and



where the starred parenthesis notation, (*), identifies the plasma-excited gases. Reaction (1) occurs when the concentration of O₂ is less than or equal to that of SiH₄, and reaction (2) when the concentration of O₂ is greater than that of SiH₄. The *a*-Si:H reaction proceeds only when electrons and noble gas ions (i.e., the plasma afterglow) are transported out of the plasma generation region into the deposition region.¹⁴ The deposition of oxides on the other hand, does not require electrons or ions to activate the heterogeneous surface deposition reaction. Our previous studies, based primarily on mass spectrometry, have demonstrated that for O₂ concentrations in He greater than about 2%, reaction (1) dominates, whereas for concentrations below about 2%, reaction (2) dominates.^{4,15} These concentrations of O₂ in He, coupled with the rate of flow of silane, represent O₂/SiH₄ gas ratios close to unity. We have generally found that high O₂ concentrations (> 2% in He), low substrate temperatures (< 200 °C), and high deposition rates (> 1 Å/s) result in IR-observable OH incorporation; whereas higher temperatures (> 250 °C), lower O₂ flow rates, and lower deposition rates (< 0.2 Å/s), minimize or eliminate any OH incorporation during the film deposition and/or the cooling down period.³ However, upon prolonged exposure to atmospheric moisture, generally on a time scale of months or years, even

these films can sometimes display measurable IR absorption in the Si-OH band.

There are two possible types of pathways by which Si-OH groups can be incorporated into the SiO₂ films; these are (i) intrinsic and (ii) extrinsic pathways.⁶ The intrinsic pathways are associated with the heterogeneous chemical reactions responsible for film growth. Extrinsic pathways refer to mechanisms after film growth has stopped, and can occur during cooling down in the deposition chamber, or outside of the chamber upon prolonged exposure to atmospheric water vapor. An earlier study by Pliskin¹⁶ has shown that Si-OH groups can be incorporated in thermal chemical vapor deposition oxides by extrinsic processes, i.e., upon exposure to atmospheric water vapor. Under all of the deposition conditions we have investigated to date, no evidence has been found to support an intrinsic OH incorporation process that occurs during film deposition as we had originally proposed.^{4,5} Our experiments have on the other hand isolated two different extrinsic pathways; the first occurring during the samples cooling down in the deposition chamber, and the second occurring outside of the chamber. These are distinguished by different IR spectroscopic signatures.⁶

III. EXPERIMENTAL EQUIPMENT AND PROCEDURES

The deposition chamber for this study has been discussed in detail in Refs. 4 and 6. We show a schematic diagram of a portion of this system in Fig. 1. To produce the SiO₂ films, a mixture of O₂ in He flowing at a total flow rate of 100 standard cm³/min (sccm), is rf excited (13 W at 13.6 MHz), with the chamber pressure maintained at 300 mTorr during deposition. A mixture of 10% silane, SiH₄, in Ar is injected through the gas dispersal ring at a rate of 10 sccm, and is not directly in contact with the plasma afterglow since the grid is maintained in its floating bias mode, thereby containing the plasma afterglow.^{4,6} The plasma-excited gas mixture can varied between an O₂ concentration of 0.5% and 100%, and yield SiO₂ thin films over this entire range.^{4,5} The substrate is positioned immediately downstream from the gas dispersal ring where the SiH₄/Ar mixture is injected. The substrate, {100} *n*-type Si with a resistivity 10–70 Ω cm, is typically heated to a temperature (*T_s*) of 200 °C. While several films were deposited for this study, only two samples were studied in detail, those designated as AOY42 and AOX89. The de-

position conditions for these films are given in Table I. Sample AOY42 was monitored by IR seven times in the first 36 hours, and the final IR measurement was made three weeks after deposition. The IR spectrum was taken for sample AOX89, daily for the first five days. This sample was then subjected to a deionized (D.I.) water boil for 30 minutes and measured. Then after three weeks it was furnace annealed and measured immediately after, and then again 90 days later. In all of the above studies, the primary postdeposition measurements were IR transmission scans between 4000 and 180 cm⁻¹, made with a Perkin-Elmer PE983 double-beam IR spectrophotometer.

IV. EXPERIMENTAL RESULTS

Figure 2 shows representative IR absorption spectra for samples deposited by remote PECVD at substrate temperatures of 100 °C and 200 °C. The 200 °C spectrum shows features at 1060, 810 and 445 cm⁻¹, corresponding respectively to the fundamental Si-O bond-stretching (*s*), bond-bending and bond-rocking modes. The absence of any feature at 3600 cm⁻¹, the OH(*s*) band, indicates that the Si-OH level is below IR detectable limits, $< 5 \times 10^{19}$ cm⁻³. The 100 °C IR spectrum shows essentially the same Si-O features as the 200 °C sample, but with an additional weak absorption at 3600 cm⁻¹, that indicates the presence of a higher concentration of Si-OH groups. There are some other small changes in the frequencies and widths of the three fundamental Si-O features that occur in this sample; these are discussed in more detail below.

Figure 3 shows a typical spectrum for a film that was deposited specifically for this study, sample AOX89, and that contains a large amount of bonded hydrogen in Si-OH groups. It shows all three of the fundamental Si-O features. We first observe that the SiO(*s*) spectral peak is at a higher frequency than in Fig. 2, 1064 cm⁻¹, rather than 1050–1055 cm⁻¹, and further that the full-width at half-maximum (FWHM) is 82.3 cm⁻¹, rather than in excess of 90 cm⁻¹, as in Fig. 2. The internal O-H bond-stretching feature, OH(*s*), of the Si-OH group, at approximately 3600 cm⁻¹, is clearly evident. This band is asymmetric with a sharp spectral cutoff, of the order of 50 cm⁻¹, on the high wavenumber side of the spectral peak, and with a more gradual cutoff on the low wavenumber side extending to about 200 cm⁻¹ below the spectral peak. There appears to be a broad symmetric feature superimposed on the asymmetric feature as well, centered about 3350 cm⁻¹. This will be established later on by a spectral subtraction process. There is also an additional absorption feature at approximately 925 cm⁻¹, that is not present in the spectra displayed in Fig. 2. Finally, there is no evi-

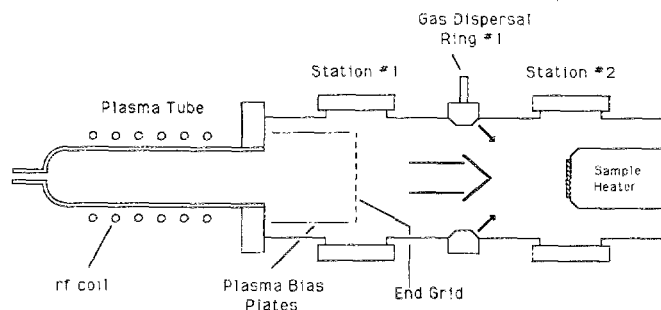


FIG. 1. Diagram of remote PECVD chamber used in this study.

TABLE I. Deposition conditions for remote PECVD SiO₂ films.

Sample	He (sccm)	O ₂ (sccm)	10%SiH ₄ + Ar (sccm)	Power (W)	<i>T_s</i> (°C)	<i>t_{dep}</i> (min)
AOX89	90	10	5	18	250	21
AOY42	90	10	10	13	200	4

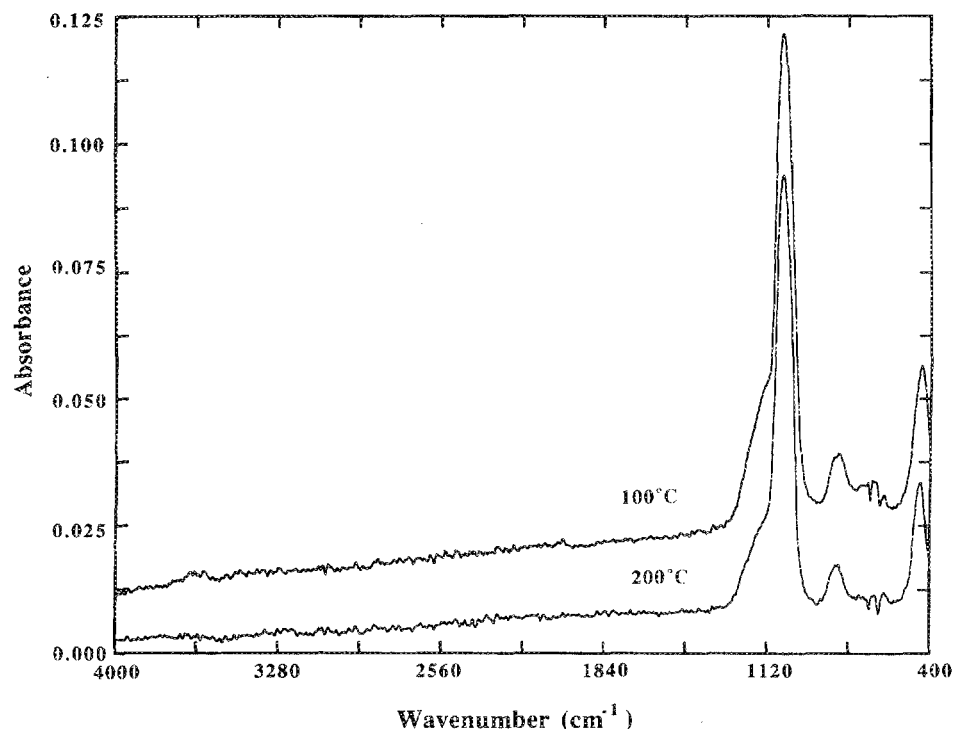


FIG. 2. IR spectra of SiO₂ thin films deposited by remote PECVD.

dence for absorption bands at either 2260 cm⁻¹ or at 875 cm⁻¹ in the spectra in Fig. 3, or either of the two spectra in Fig. 2. These two absorptions are the spectral features associated with the bond-stretching and bond-bending vibrations, respectively, of Si-H groups in an SiO₂ host network,¹⁷ and for films produced by remote PECVD, and as mentioned above are generally only found in hydrogenated suboxides.¹⁷

Figure 4(a) shows the IR spectra of the second SiO₂ film, AOY42, in the low wavenumber region, 1400 to 400 cm⁻¹, and Fig. 4(b) shows the spectra in an expanded region in the vicinity of the 1060 cm⁻¹ band, from 1275 to 950 cm⁻¹. These spectra illustrate the changes that occur with increasing exposure to atmospheric water, and increasing incorporation of Si-OH bonding groups resulting from the reactions between this atmospheric water vapor and the intentionally

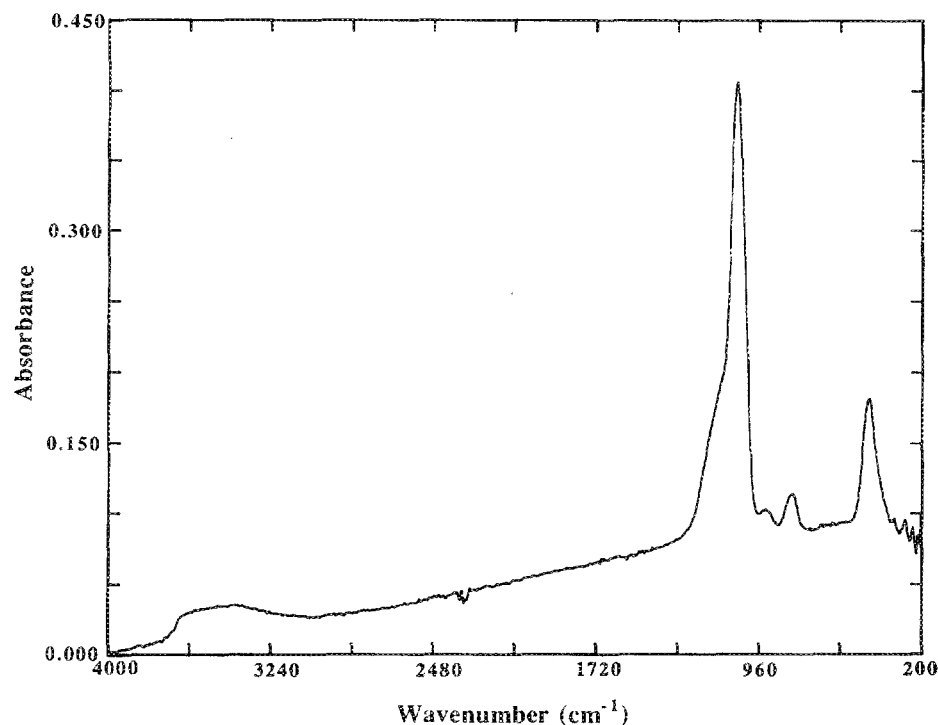


FIG. 3. IR spectrum of a remote PECVD SiO₂ film especially deposited for this study. This spectrum was taken after five days of exposure to atmospheric ambient.

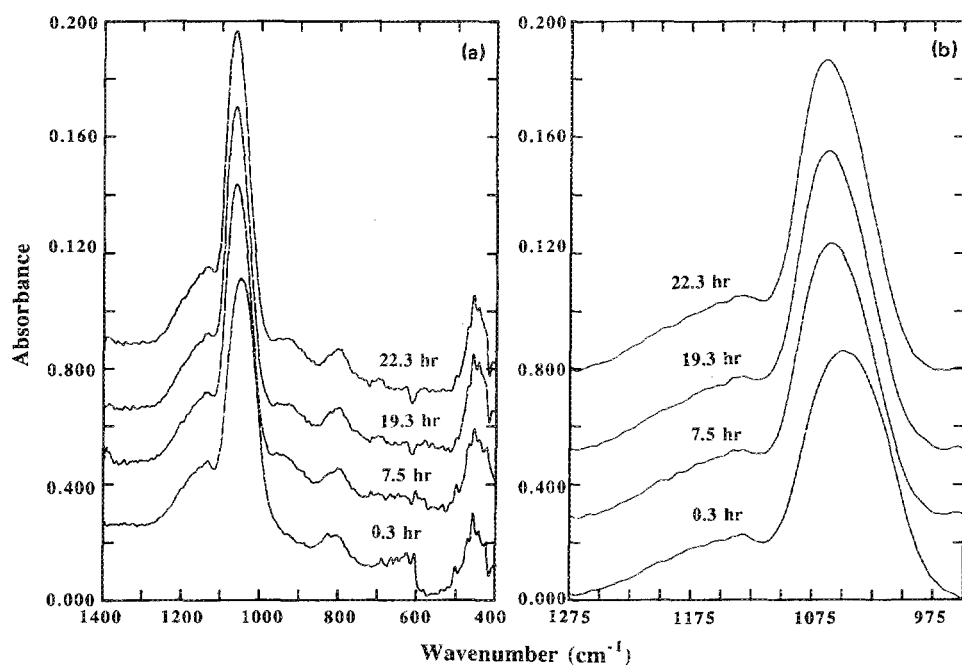


FIG. 4. (a) Changes in the 1400–400 cm^{-1} region of the IR spectrum on exposure to atmospheric water. (b) Magnified spectrum in the vicinity of the SiO(s) band.

hygroscopic SiO₂ thin film. The spectral peak of the SiO(s) band shifts from an as-deposited value of 1050 cm^{-1} to 1065 cm^{-1} after this prolonged exposure to atmospheric water. The position of this spectral peak has ranged from 1042 cm^{-1} in as-deposited samples that were spectroscopically free of Si-OH groups, to 1072 cm^{-1} in films that have had the most prolonged exposures to atmospheric water vapor. Returning to Fig. 4(b), the FWHM decreases significantly as the peak position shifts to a higher wave number from the as-deposited value of 82 to 68 cm^{-1} , after the prolonged exposure to atmospheric water vapor. The range of FWHM for all samples we have studied is from an as-deposited value of 92 to 66 cm^{-1} in films exposed to atmospheric water for

long periods of time. The integrated absorbance at the spectral peak of the SiO(s) band increases as the position and FWHM shift, from the as-deposited value of 16 600 to 19 800 cm^{-1} , after prolonged exposure to water vapor. Though not clearly demonstrated by the spectra for the sample in Fig. 4(b), the high-wavenumber shoulder of the SiO(s) band has also been observed to increase relative to the SiO(s) peak height.⁶

Figure 5(a) shows the evolution of the band at 3600 cm^{-1} , OH(s), for different time intervals for sample AOY42; this is the same sample as in Figs. 4(a) and 4(b). The first spectrum, taken at about 20 min after removal from the chamber, shows the distinct asymmetric character dis-

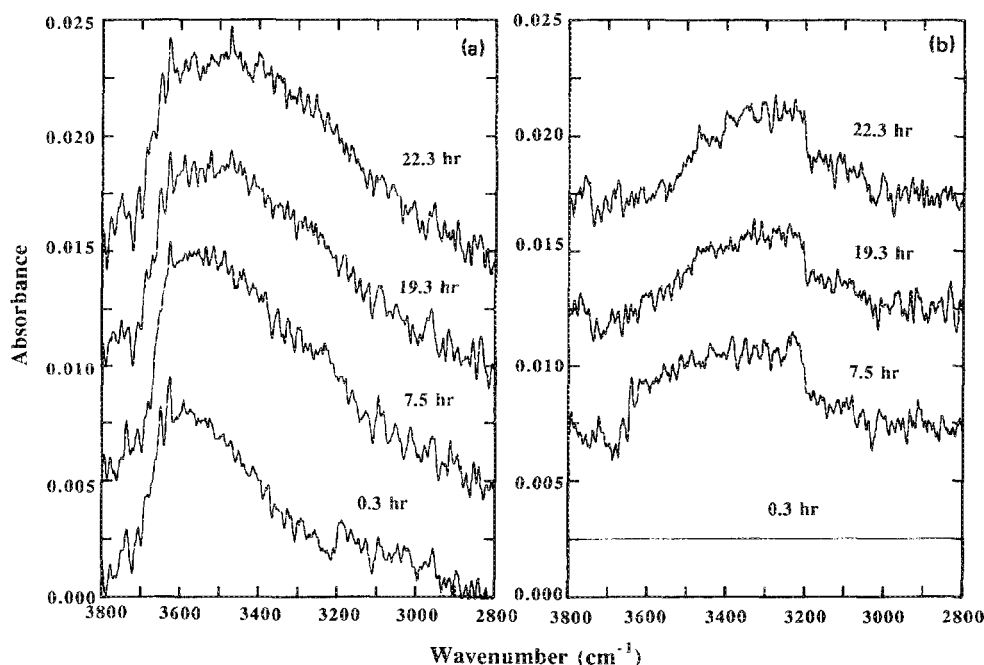


FIG. 5. (a) Evolution of the OH(s) band on exposure to atmospheric water. (b) Evolution of the 3350 cm^{-1} feature. This plot was made from a subtraction of the initial IR spectrum from subsequent spectra.

cussed above with reference to Fig. 3, and hereafter designated "the 3650 cm⁻¹ band." Upon exposure to atmospheric water, the asymmetric feature does not significantly change, but a new and symmetric feature begins to emerge from the 3650 cm⁻¹ band. Fig. 5(b) is the difference between the initial spectrum and the subsequent spectra. By the third spectral subtraction, it is clear that the new band has a more symmetric character. We designate this feature as "the 3350 cm⁻¹ band." The very abrupt discontinuity in the spectrum at 3200 cm⁻¹ is an artifact of the infrared spectrophotometer, and not a characteristic feature of this band.

The 925 cm⁻¹ feature appears only in samples which show absorption associated with the internal O-H bond-stretching modes of Si-OH group. Figure 6 includes plots of the integrated absorption of the 925 cm⁻¹ band versus the integrated absorption strength of the entire OH(s) band, including both the 3600 and 3350 cm⁻¹ subband together [Fig. 5(a)], and the 3350 cm⁻¹ subband only [Fig. 5(b)]. This plot shows a linear relationship between the two integrated absorptions. A linear regression analysis provides a fit for both curves with slopes of 6.6×10^{-2} , and correlation coefficients of 0.82. The x -intercept absorbance for the summation of both subbands is about 3100 cm⁻². A linear relationship is also obtained for the 3350 cm⁻¹, but the x intercept is now at the origin ($x = 0$). The $x = 0$ intercept of the 925 cm⁻¹ absorbance versus the 3350 cm⁻¹ absorbance indicates a correlation between these two spectral features, whereas the positive nonzero correlation for the other case indicates that the 925 cm⁻¹ feature and 3650 cm⁻¹ band are not associated with the same local bonding groups. Similar behavior has been found for data we have obtained from other hygroscopic SiO₂ films that were deposited under a wide range of different gas flow conditions with O₂ plasma gas fraction ranging from 0.5% to 100%.

The spectral character of the SiO(s) band exhibits systematic changes that correlate with exposure time, and hence with the changes in the character of the OH(s) band that have been described above. Figure 7 shows that position of the spectral peak increases from 1050 to 1065 cm⁻¹, and that

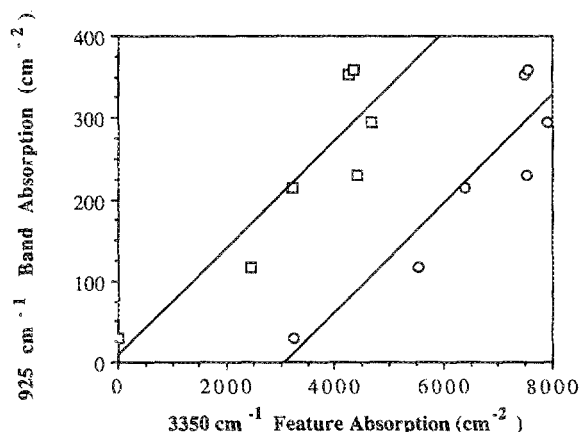


FIG. 6. Plot of the 925 cm⁻¹ integrated absorption against (a) the OH(s) integrated absorption (O); and (b) difference between the initial and subsequent OH(s) integrated absorptions (□).

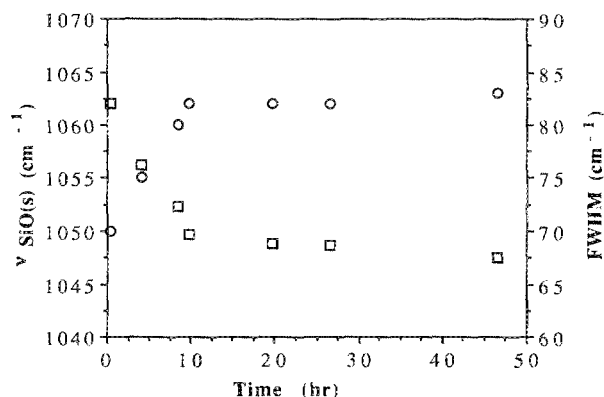


FIG. 7. (a) Plot of the change in SiO(s) peak frequency (O) as a function of time of exposure to the atmosphere after film deposition. (b) Plot of the change in the SiO(s) FWHM (□) against time of exposure to the atmosphere after film deposition.

the FWHM decreases from 82 to 68 cm⁻¹ as the exposure time increases. The majority of these changes occur within ten hours of the removal of the sample from the chamber, though measurable changes could also be detected as long as three weeks later. For comparison, fully relaxed thermal oxides have average spectral peak positions about 1078 ± 1 cm⁻¹, with a FWHM ranging between 74 and 76 cm⁻¹.^{18,19}

V. DISCUSSION

The differences between the spectral character of the OH(s) bands immediately following film deposition and that character after prolonged exposure to atmospheric water vapor can be understood in terms of the local atomic environments of the Si-OH groups. The character of the vibrational modes of Si-OH groups are strongly affected by hydrogen-bonding interactions.^{20,21} In many organic materials the position of the OH(s) band shifts to lower wave-number with increasing hydrogen-bonding interactions.²² These interactions occur between the H atom of the OH group and the O atoms of the host network, as in the case of SiO₂, or the O atoms of other OH groups in alcohols and related compounds.^{20,23} The hydrogen bonding (hereafter H bonding) interaction can be represented by OH...O.²³ The H-bonding interaction is stronger between near-neighbor OH pairs, than between an OH group and the bridging O atom of Si-O-Si groups in the SiO₂ network.²¹ In addition it has been observed that as the OH...O distance decreases, the H-bonding strength increases and the frequency of the O-H stretching vibration decreases.²³ Small changes in the O...OH or equivalently the O...O distance, ~ 0.02 Å, can result in shifts as large as 50 cm⁻¹ in the OH(s) frequency.^{19,20} This then provides the basis for interpreting the differences between the asymmetric feature at 3650 cm⁻¹ and the symmetric feature at 3350 cm⁻¹ discussed above.

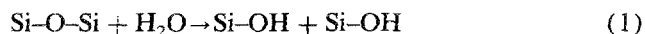
We propose that there are three possible local environments in which the Si-OH groups in an SiO₂ can exist (i) as near-neighbor Si-OH groups; (ii) as Si-OH groups that are only partially shielded from other neighboring Si-OH groups, and (iii) as Si-OH groups that are effectively isolated from other Si-OH groups by the SiO₂ network structure.

We propose that the symmetric feature at 3350 cm⁻¹ and the asymmetric feature at 3650 cm⁻¹ are associated with the extreme cases denoted above as bonding arrangements (i) and (iii). The local environment that provides the strongest H-bonding interaction is between neighboring Si-OH groups. Small changes in the distance between oxygen atoms of these groups, e.g. 0.08–0.02 Å, can easily produce respective shifts in the IR active OH(*s*) frequency as large as 50–200 cm⁻¹.²⁰ For the other extreme, where the Si-OH group is effectively isolated from other Si-OH groups by the Si-O-Si network, there is only a weak interaction between the H atom of the Si-OH group and the O atoms of the Si-O-Si network. This weak interaction establishes the high wavenumber cutoff for the band at a frequency for observed in OH groups that are virtually free of any significant H-bonding interactions, e.g., OH groups on the surface of a film.²⁰ This means that the vibrational frequencies at the high wavenumber side of the asymmetric band are primarily related to the SiO₂ network's H-bonding interactions with isolated Si-OH groups, while the rest of the band is displaced to lower wavenumbers due to H-bonding interactions with partially shielded Si-OH groups, i.e., those that are not necessarily bonded to nearest neighbor Si atoms in the network structure.

We have observed that there are two distinct spectral features that contribute to the OH(*s*) band, an asymmetric feature, 3650 cm⁻¹, and a symmetric feature, 3350 cm⁻¹, [see Figs. 5(a) and 5(b)]. From work previously published, we found that the 3650 cm⁻¹ generally develops with a time constant on the order of minutes, while the 3350 cm⁻¹ develops with a time constant on the order of hours or days upon exposure to atmospheric water.⁶ The asymmetric broadening of the 3650 cm⁻¹ OH(*s*) band derives from the existence of a continuous range of OH...O distances, from nearly isolated Si-OH groups, accounting for the absorption on the high wavenumber side of the band, to more closely associated Si-OH groups accounting for the low wavenumber tail. It has been shown that the oscillator strength for the high wavenumber absorbing configurations is about five times weaker than for the low wavenumber configurations.^{16,18,24} This leads one to conclude that the band-shape reflects a continuous, and effectively random distribution of interaction distances. The origin of the 3350 cm⁻¹ feature is different, and the symmetric character of this band suggests a different local bonding arrangement.

The slow reaction process that causes the 3350 cm⁻¹ feature develops in films exposed to atmospheric water, leading to the incorporation of Si-OH groups into the network that is very different from the incorporation of Si-OH groups that give rise to the asymmetric band at 3650 cm⁻¹. The symmetric shape suggests that the 3350 cm⁻¹ band is the result of near-neighbor Si-OH groups with a specific spatial configuration, and a narrow range of OH...O separations. The magnitude of the shift of this feature with respect to the frequency of the weakly interacting OH groups must derive from a relatively strong H-bonding interaction with neighboring Si-OH groups. Novak has determined a relation between the frequency of the OH(*s*) vibration and the O...O distance of the O atoms in the neighboring OH

groups, working with x-ray and IR data from several organic compounds.²³ Using his relationship, we find that the symmetric peak at 3350 cm⁻¹ corresponds to an O...O spacing of about 2.75 Å. This interatomic distance is consistent with the near-neighbor SiOH pairs being generated by the conversions of an Si-O-Si environment to two SiOH groups through the reaction:



The data displayed in Fig. 6 have demonstrated that the absorption at 925 cm⁻¹ is correlated only with the symmetric 3350 cm⁻¹ feature, and not with the total absorption in the Si-OH band that also includes contributions from the asymmetric 3650 cm⁻¹ feature. We propose that the strong H-bonding interaction that produces the symmetric feature in the OH(*s*) at 3350 cm⁻¹, can also account for the 925 cm⁻¹ vibrational mode. We interpret this feature as being due to a coupled mode that combines stretching displacements of the entire OH group relative to the Si atom with internal bending displacements of the OH group. This interpretation derives from the application of a simplified force-constant model. Hydrogen bonding interactions contribute significantly to the short-range forces involved so that the particular frequency of this combined or coupled motion is correlated with the strong H-bonding interactions of the same near-neighbor Si-OH groups that contribute to the symmetric O-H feature at 3350 cm⁻¹.

We noted earlier that the films used in this study are particularly susceptible to postdeposition OH incorporation, because they have a large fraction of highly distorted Si-O-Si bonds which are inherently more reactive than relaxed Si-O-Si bonds. It has been shown that the chemical reactivity of Si-O-Si groups is the greater, the smaller the bond angle at the oxygen vertex.⁹ Silicon dioxide films produced by remote PECVD have bond angles at the O atom sites that are considerably less than those of oxides that are formed by the thermal oxidation of Si; this observation derives from the position of the spectral peak in the SiO(*s*) band.

As the Si-O-Si bond angle decreases, the Si-O-Si group becomes more reactive, and the attack of these groups by water converts them to near-neighbor Si-OH groups. If we assume that the spectral width of the Si-O band derives from a distribution of Si-O-Si bond angles, then the low wavenumber side of this band (i.e., at wave numbers below the spectral peak) is associated with the most reactive bonds. This is consistent with the shift of the SiO(*s*) spectral peak to higher wavenumbers in the films which have been attacked by water vapor and consequently display the symmetric OH(*s*) feature and the 925 cm⁻¹ absorption as well. The decrease in the FWHM of the SiO(*s*) feature is a subtractive effect and results from the removal of the low wavenumber side of the band.

The position of the spectral peak of the SiO(*s*) band has been correlated with the Si-O-Si bond angle.^{25,26} As shown in Figs. 4(a) and 4(b), the spectral peak of the SiO(*s*) vibration of the as-deposited or initial spectrum is at approximately 1056 cm⁻¹, whereas the spectral peak of the same band in thermally-grown and relaxed oxides is at 1078 ± 1 cm⁻¹.¹⁶ This Si-O-Si bond angle is ~144° in relaxed thermal oxides,

and is generally about 7–10° smaller in the as-deposited remote PECVD oxides. The greater reactivity of these bonds in the remote PECVD oxides has been demonstrated by higher etch rates in buffered HF.²⁷ This means that as-deposited films contain a significant fraction of reactive bonds, and have a porosity that allows for a rapid in-diffusion of small molecules and ions.

Therefore there are the three spectral changes that are correlated: (i) the development of a symmetric 3350 cm⁻¹ OH(*s*) feature; (ii) the emergence of a band at 925 cm⁻¹; and (iii) the shift of the spectral peak of the SiO(*s*) band to a higher wavenumber which is accompanied by a decrease in the FWHM of this same band. All of these spectral changes can be explained by the attack of Si-O-Si groups by atmospheric water. This attack results in near-neighbor pairs of Si-OH configurations, which in turn display significant hydrogen bonding interactions. The bands at 3350 and 925 cm⁻¹ are related to the near-neighbor Si-OH pairs, and the changes in the SiO(*s*) stretching band derive from the attack of the more reactive Si-O-Si groups that comprise the low wavenumber side of the SiO(*s*) absorption band.

In summary, we have found that under special circumstances it is possible to grow, by remote PECVD, SiO₂ films that are hygroscopic. We have identified two distinct reactions by which OH may be incorporated into the films: (i) a fast reaction that occurs on the order of minutes, and produces an asymmetrically shaped OH(*s*) band at 3650 cm⁻¹; and (ii) a slow reaction that occurs on the order of hours or days and produces a symmetrically shaped OH(*s*) band centered about 3350 cm⁻¹. The differences in the center frequencies of these bands reflect differences in H-bonding interactions. The symmetric feature is associated with near-neighbor Si-OH groups that promote a relatively strong H-bonding interaction, whereas the asymmetric feature is associated with a isolated, as well as weakly interacting Si-OH groups with a continuous distribution of H-bonding interactions.

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