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Structural investigation of silica gel films by infrared spectroscopy

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Fourier transform infrared absorption spectroscopy has been utilized to characterize the structure of porous silica gel films, both deposited on *c*-Si substrates and free standing. The films were either dried at room temperature or subjected to partial densification at 400–450 °C. The spectra of the gel films are compared to those of thermal SiO_2 grown on *c*-Si and to Kramers–Kronig analysis of the reflection spectra of bulk SiO_2 gels and *v*-SiO_2. The gel films show small frequency shifts compared to the latter spectra and they also exhibit new bands due to the presence of OH groups, although very little molecular water or residual organic species were found. The results are interpreted in terms of the gel structure. Compared to the thermal oxide, the sharp peak near 1070 cm^{-1} is narrower for the gels and the spread in intertetrahedral angles is estimated at 24° and 27° for room temperature dried and partially densified gels, respectively, compared to 33° for the thermal oxide. This is in agreement with a state of strain in the Si—O—Si bridges of the gels near the surface of the pores. The gel films have also a stronger shoulder near 1200 cm^{-1}, whose intensity decreases with heat treatment of the gel. Its nature is related to the longitudinal optical (LO) component of the high-frequency vibration of SiO_2 and it is suggested that the gel pores may account for the activation of the LO component.

I. INTRODUCTION

The properties of amorphous SiO_2 (*a*-SiO_2) films on single crystal Si (*c*-Si) substrates are very important from a technological viewpoint, given their application in the electronics industry. A typical example are the metal-oxide-semiconductor (MOS) devices which make use of a thermally grown *a*-SiO_2 layer on *c*-Si substrates, whose quality is highly relevant to the device performance. The structure of the oxide layer and the nature of the SiO_2/Si interface have been extensively discussed in a review by Pliskin[1] and in other recent publications.[2–8] In addition to thermal oxidation, *a*-SiO_2 films may also be deposited by several other methods such as sputtering,[1] electron beam evaporation,[9] thermal decomposition of alkoxysilanes,[1] chemical vapor deposition (CVD)[8] and by the sol-gel method using spin-on solutions which are commercially available or may be prepared in the laboratory.[10] The sol-gel method is especially attractive in semiconductor technology.[10]

There is still considerable disagreement about the structure of SiO_2 films and the SiO_2/Si interface, even in the most studied case of the thermal oxide, namely, concerning the existence of bond strain[3,4,6] and microvoids.[7] In addition, although the infrared (IR) spectra of such films have been extensively recorded, the lower frequency features have seldom been discussed and there is no agreement as to the exact structural significance of the high frequency peaks occurring between ~ 1000 and 1260 cm^{-1}. Although these features are generally accepted to arise mostly from antisymmetric stretching vibrations of Si—O—Si bridging sequences,[11] different interpretations still hold. Galeener[12] attributed the partially resolved pair of peaks in the reflectivity spectrum of bulk *v*-SiO_2 to an antisymmetric stretching of the bridging oxygens parallel to the Si-Si direction plus some Si cation motion, which could be resolved via Kramers–Kronig analysis into transverse optical (TO) and LO components arising from long-range Coulomb coupling. The TO component involves nonzero derivatives, at the equilibrium internuclear configuration, for dipole moment components perpendicular to the propagation vector **k** of the phonon waves, whereas the higher-frequency LO component involves dipole moment changes parallel to **k**.

In the case of thermal SiO_2 films, Boyd[5] suggested the occurrence of some shorter bonds within each SiO_4 tetrahedron in order to explain a slightly asymmetric peak near 1080 cm^{-1}, typical of the IR transmission spectra of thin films (3–45 nm thick) which did not exhibit the high-frequency shoulder of thicker films at ~ 1200 cm^{-1}. On the other hand, Hubner *et al.*[2] used IR transmission at oblique incidence (55° off-normal) and they were able to detect the TO and LO components simultaneously, at 1091 and 1260 cm^{-1}, respectively, for 500-nm-thick thermal SiO_2 films. Olsen and Shimura[8] used multiple internal reflectance (MIR) at 60° off-normal incidence with linearly polarized light and they were able to detect, in 3-nm-thick thermal SiO_2 films, the TO and LO components at 1080 and 1240 cm^{-1}, using parallel polarized (*p*) light, whereas perpendicular polarized (*s*) light detected essentially only the TO mode. (For *p* light, the electric vector lies in the reflection plane, whereas for *s* light it is perpendicular to this plane). The same authors[8] apparently observed also the TO and LO components of the high-frequency mode in

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10-nm-thick SiO_2 films deposited by CVD on c-Si, but at somewhat lower frequencies, near 1060 and 1200 cm^{-1}, respectively. However, they were not able to detect the LO component for 6 nm thick spin-on SiO_2 films which were dried at an unspecified temperature but not cured, presumably because the spin-on film did not have a completely cross-linked continuous network structure[8]. The MIR spectrum of the uncured spin-on glass was similar to the transmission spectrum of thermal SiO_2 at normal incidence, for both s and p polarized IR light.

In the case of gels, Kuisl[10] deposited SiO_2 films on c-Si substrates from spin-on solutions by the sol-gel method and he studied physical properties such as viscosity, thickness and densification behavior; he also mentioned that the high-frequency transmission peak occurred at $\sim$ 1075 cm^{-1} for annealing temperatures $\leqslant$800 °C, whereas it increased up to 1085 cm^{-1} for annealing above 800 °C. Recently, Almeida *et al.*[13] have characterized porous, alkoxide-derived bulk silica gels, either dried at room temperature or subjected to partial densification at 400 °C, by IR reflection spectroscopy, with Kramers–Kronig analysis of the data. The high-frequency reflection peak of v-SiO_2 at 1125 cm^{-1} was shifted to lower frequency by as much as 40 cm^{-1} in room temperature dried gels and major differences were found for the LO component of this vibrational mode, which was broader and had a lower frequency in the gels. Simple calculations showed that the observed behavior could in part be due to a certain degree of strain in the Si—O—Si bridging bonds near the surface of the gel pores, with larger bridging angles and longer Si—O bonds, the latter effect being predominant.[13]

In the present paper, FTIR absorption spectra are presented for porous SiO_2 gel films and they are compared to IR spectra of thermal SiO_2 films and to reflection spectra of bulk porous SiO_2 gels deconvoluted by Kramers–Kronig methods. The gel films are spin-coated on single-crystal silicon wafers polished on one side, in order to obtain smooth films of reasonable and uniform thickness on an IR-transparent substrate. The catalyst and pH conditions have been chosen in a way to obtain continuous polymeric gel structures and slow hydrolysis rates before the spinning process. The structure of the gel films is discussed based on the IR results, which are able to provide some insight into the unique features of gel films. The nature of the shoulder near 1200 cm^{-1} is also discussed in detail.

II. EXPERIMENT

Starting solutions were prepared by mixing 20 ml of tetraethoxysilane (TEOS, Morthon Thiokol, 99%), 40 ml of ethanol (200 proof) and 20 drops of 1N HCl solution at room temperature, adding 25 ml of distilled water (four times the theoretical amount needed for hydrolysis), heating with stirring up to $\sim$ 70 °C and cooling to room temperature, with a final pH near 2.5. The spin-on solutions were prepared by diluting these silica sols 1:1 in ethanol. Thin silica gel films were spun on single crystal silicon wafers from five drops of aged spin-on solution, using a Headway Research photoresist spinner (mod. 1-EC101D) at 2500 rpm, for 15 s. The Si wafers were n-type ⟨100⟩ or ⟨111⟩ Czochralski ($\rho \sim 1\ \Omega$m), 200 μm thick, polished on one side and chemically cleaned (H_2O_2/H_2SO_4, distilled water rinse, HF, rinse, H_2SO_4 and rinse, all at room temperature). Thermal SiO_2 films were grown in dry oxygen at $\sim$ 1000 °C. A few free standing SiO_2 gel foils were also prepared by letting small amounts of silica sol to gel and dry on shallow plastic Petri dishes or glass test tubes. Most silica gel films were either dried at room temperature in a dessicator for at least two weeks or they were heat treated in air for 3 hours at 450 °C, in a tube furnace. This heat treatment did not lead to the formation of thermal oxide on the wafer side opposite to the spin-on deposit.

TABLE I. Thickness and refractive index at $\lambda = 632.8$ nm of silica gel films dried under different conditions.

Film designation	Drying conditions	Thickness (nm)	Refractive index
A_t	Thermal oxide	110	1.464
B	Thermal oxide	127	1.461
C_0	Room Temp.	167	1.427
D_0	Room Temp.	204	1.405
E_0	Room Temp.	212	1.401
F_0	Room Temp.	$\sim$212	$\sim$1.40
G_0	Room Temp.	61	1.435
D_1	450 °C, 3 h	155	1.429
E_1	450 °C, 3 h	159	1.429
H_1	400 °C, 3 h	149	1.438
Bare Si wafer	···	200 μm	3.876
Gel foil	Room Temp.	$\sim$1 μm	···

The thickness and refractive index ($\lambda = 632.8$ nm) of the films deposited on c-Si substrates were measured by ellipsometry with a Rudolph Research Automatic Ellipsometer (AutoEL-III).

IR spectra were recorded down to 400 cm^{-1} in an evacuated IR/98 FTIR spectrometer equipped with a KBr beamsplitter and a DTGS detector, with 4 cm^{-1} resolution, at room temperature. Spectra were taken in the absorption mode (normal incidence), with natural light. These spectra often exhibited closely spaced interference fringes due to the 200 μm thick c-Si substrates and those were sometimes attenuated with a smoothing routine.

III. RESULTS AND DISCUSSION

In the case of dilute TEOS solutions, using acid catalyzed hydrolysis, polycondensation reactions are severely limited. It is primarily the rapid evaporation of the solvent during film deposition (here through spinning) that leads to the condensation of a porous gel film. It is likely that the film structure is strongly dependent upon the molecular weight distribution of the oligomers present in the solution. Thus, even after drying at room temperature, silanol (Si—OH) groups, molecular water and ethanol remain in the gel network to some extent. Fully dense SiO_2 films are only produced after heat treatment at temperatures between 800 and 1200 °C.

Table I gives thickness and refractive index values for gel films dried under different conditions and also for thermal oxide films, a bare reference Si wafer and a free standing gel foil. The subscript 0 refers to room temperature

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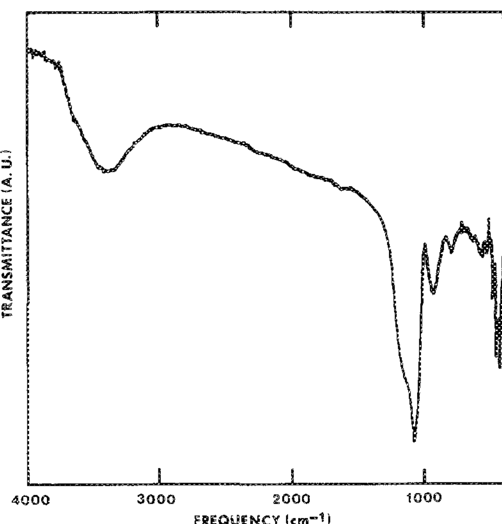

FIG. 1. FTIR transmission spectrum of film F_0, referenced to a bare Si wafer.

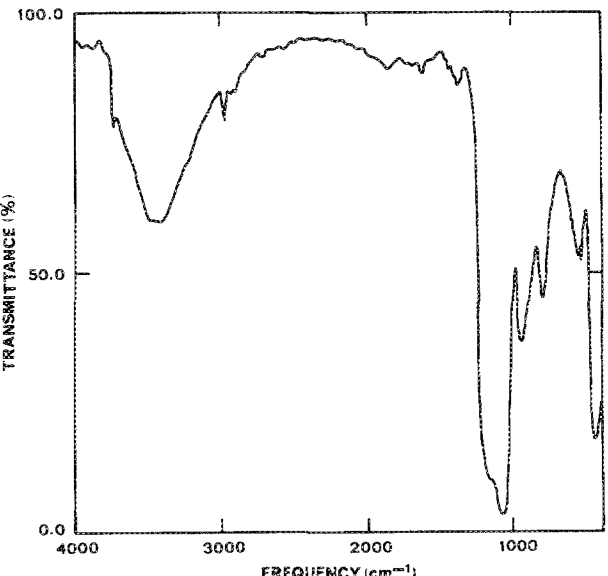

FIG. 2. FTIR transmission spectrum of a free standing silica gel foil.

drying, whereas 1 refers to a heat treatment near 450 °C. Samples D and E were tested under two different drying schedules, for comparison. It was observed that relatively thick, room temperature dried gel films such as D_0 and E_0 had refractive indices ~0.06 lower than the fully dense thermal oxide (A_t and B_t), due to porosity. Thinner films such as C_0 and especially G_0 dried faster and became denser, with indices only ~0.03 lower than the thermal oxide. After a heat treatment at 450 °C, samples D_1 and E_1 decreased in thickness by ~25%, whereas their refractive index increased ~0.03 up to ~1.43, still ~0.03 less than dense silica glass. (A piece of dense, bulk v-SiO_2 had a refractive index measurement of 1.459 with the same ellipsometer and the slightly higher index measured for the thermal oxide may be indicative of some residual compressive stresses).[14]

The IR spectra of all the gel films are compared, whenever possible, to those of thermal SiO_2 and the room temperature dried, free standing SiO_2 gel foil. Figure 1 shows the transmission spectrum of sample F_0 referenced to a bare Si wafer, which was typical of all the room temperature dried gel films. Figure 2 shows a similar spectrum for the free standing gel foil, whose thickness was not measured but was probably of the order of 1 μm, since the approximate penetration depth of 10-μm IR light into bulk v-SiO_2 (absorption coefficient $\alpha \sim 4\times10^4$ cm^{-1}) is roughly 0.2 μm.[15] Both spectra exhibit a O–H stretching region peaking at ~3400 cm^{-1}, where some freely vibrating OH groups (high-frequency shoulder) and a majority of hydrogen-bonded OH groups[16] are apparent. Only a very weak peak near 1650 cm^{-1} is observed for both spectra, which could in part be due to residual ethanol, indicating that very little molecular water, if any, remained in the gels at this stage (molecular water has a deformation band near 1630 cm^{-1}). The gel foil exhibits a sharp peak at 3740 cm^{-1}, due to free surface silanol groups[17] and it also shows small residual features near 2900–3000 cm^{-1} due to organic residues (alcohol or TEOS). The spectrum of the spun film (Fig. 1) does not reveal any significant amount of residual organic species. Figure 3 shows in detail the Si–O fundamental region for film C_0 (with the spectrum of the gel foil superimposed) and Fig. 4 shows the corresponding spectrum for the thermal oxide films A_t and B_t, grown on opposite sides of the same wafer. Both gel spectra exhibit bands centered near 940–960 cm^{-1} and 578 cm^{-1} which are absent in the thermal oxide. The higher-frequency peaks may be attributed to stretching vibrations of Si—OH or Si—O$^-$ groups,[13] whereas the lower-frequency peak may tentatively be associated with rocking motions of the same species. Also, the gel samples

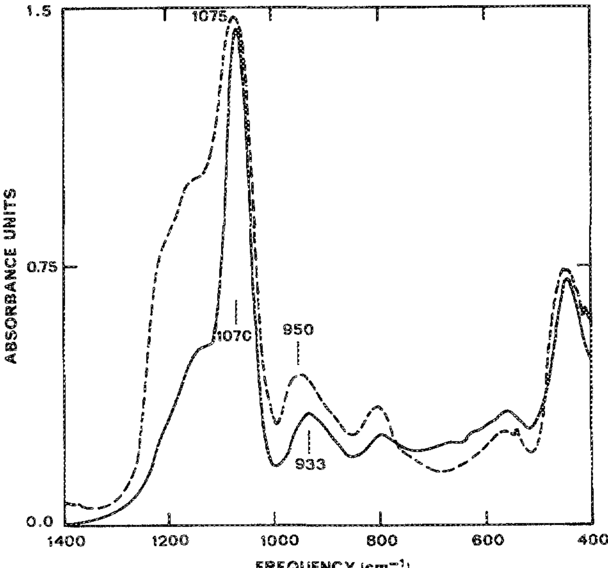

FIG. 3. FTIR absorption spectra of film C_0 (full curve) and a free standing gel foil (dashed curve), in the fundamental Si—O region.

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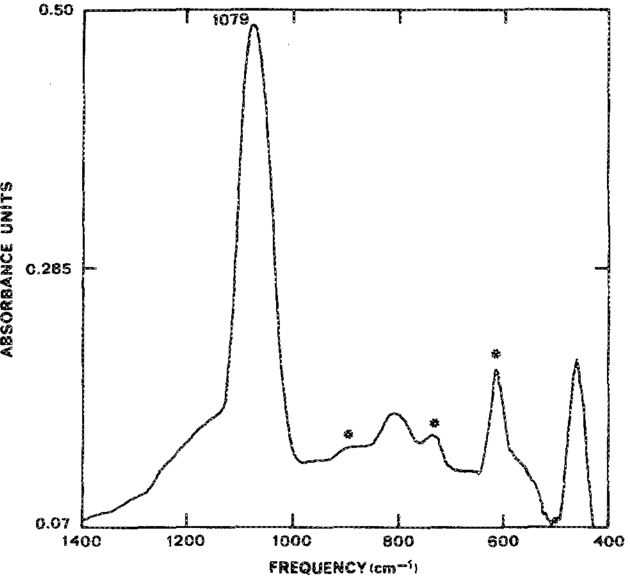

FIG. 4. FTIR absorption spectrum of thermal oxide films A_t and B_t grown on the same Si wafer. (The peaks marked with a * were due to incomplete subtraction of the c-Si substrate).

have a much more pronounced shoulder on the high-frequency side of the dominant Si—O—Si stretch near 1075 cm^{-1} and this shoulder, located in the vicinity of 1200 cm^{-1}, is very strong in the thicker gel foil. In addition, with the exception of the 1075 and 578 cm^{-1} peaks, all the other features in the spectrum of the gel foil are stronger, relatively to the dominant peak, compared to the other two spectra of Figs. 3 and 4, whereas they generally appear weakest in the thermal oxide spectrum. Figure 5 shows the fundamental Si—O spectrum for the partially densified film H_1, where it is clear that these vibrational features have intensities intermediate between those of the

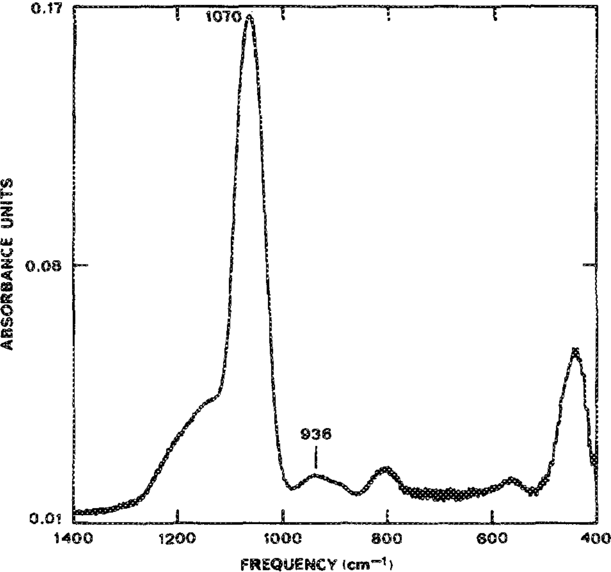

FIG. 5. FTIR absorption spectrum of film H_1, in the fundamental Si—O region.

room temperature dried gel film of Fig. 3 and the thermal oxide films of Fig. 4.

According to Galeener,[12] the three dominant features in the spectra of the partially densified gels or the thermal oxide, which are characteristic of bulk v-SiO_2, may be assigned as follows: the lower-frequency band near 450 cm^{-1} is due to rocking motions of the oxygen atoms perpendicular to the Si—O—Si plane, accompanied by some Si cation motion; the intermediate frequency band near 800 cm^{-1} is atributted to symmetric stretching motions of the oxygen atoms along the bisector of the Si—O—Si bridging angle θ, with some Si cation motion; the high-frequency dominant band near 1070 cm^{-1} is due to antisymmetric stretching of the oxygen atoms along a direction parallel to Si—Si, accompanied by a substantial amount of cation motion.

Part of the absorption losses apparent in Figs. 1–5 stem from sample reflection and this phenomenon leads to some distortion of the absorption bands due to anomalous dispersion of the refractive index.[18,19] For porous samples such as the gels, some scattering losses may also occur, particularly for shorter wavelengths closer to the pore size (the actual pore size distribution was not measured in this work). In order to obtain correct values for the fundamental optical constants, the best method is perhaps Kramers–Kronig analysis of reflectivity data at near normal incidence such as performed by Galeener *et al.*[20] on v-SiO_2, v-GeO_2, and v-BeF_2 at ~ 20° off normal. Those authors obtained TO and LO spectra for these glasses, corresponding to maxima in the imaginary part ϵ_2 of the dielectric constant ($\epsilon^* = \epsilon_1 + i\epsilon_2$) and in the energy-loss function $\mathrm{Im}(-1/\epsilon^*)$, respectively. Although Phillips[21] has argued against such interpretation, the initial observations of Galeener and Lucovsky,[22] concerning LO-TO splittings in v-SiO_2 and v-GeO_2, have been theoretically confirmed by Payne and Inkson[23] and de Leeuw and Thorpe.[24] Within this framework, all the three major vibrational modes of v-SiO_2 exhibit TO-LO splittings, of magnitudes 49, 17, and 180 cm^{-1}, in order of increasing peak frequencies, respectively.[22]

Almeida *et al.*[13] compared TO and LO spectra of bulk porous SiO_2 gels with those of bulk v-SiO_2 and they found that the TO spectra were quite similar, with nearly identical peak frequencies, whereas the LO spectra showed major differences. Figures 6 and 7 compare the TO and LO spectra, respectively, for bulk porous SiO_2 gel and bulk v-SiO_2. By comparing these two figures with the spectra of Figs. 3 and 4, it is observed that the TO frequencies always fall very close to the absorption frequencies. Since the high frequency, dominant absorption band near 1070 cm^{-1} always showed the largest TO-LO splitting and the shoulder on the high-frequency side of this band lies near the position of the LO mode, we will concentrate on this high-frequency band in the discussion that follows. The peak near 1070 cm^{-1} will henceforth be designated by TO and the shoulder by SH, for the sake of simplicity.

Because electromagnetic waves are transverse, IR radiation can be absorbed by the TO phonons of an infinite (thick) solid, but not by the the LO phonons. However,

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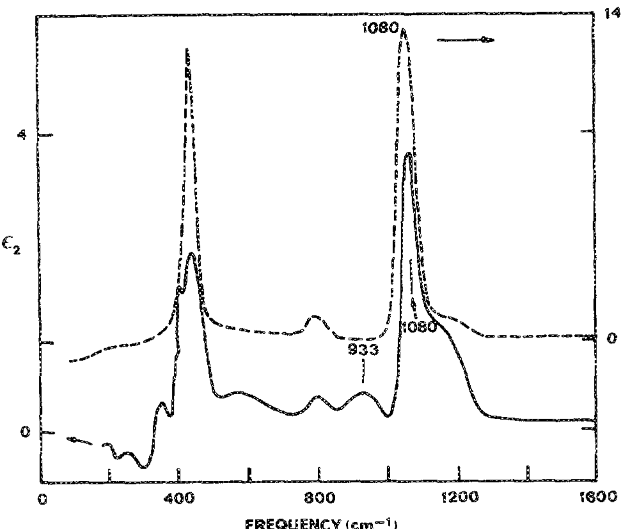

FIG. 6. Infrared dielectric constant ϵ_2 (TO spectrum) of bulk porous SiO_2 gel (full curve) and bulk v-SiO_2 (dashed curve). (Adapted from Ref. 13.)

Berreman[25] argued that crystalline films which are thin compared to the IR wavelengths will have TO vibrations parallel to the film surface and LO vibrations perpendicular to it, such that radiation incident normal to the surface (as in conventional IR transmission spectroscopy) will only excite TO modes, whereas the p polarized component of radiation incident obliquely to the surface will have electric field components both parallel and normal to the surface, thus interacting with both TO and LO modes, respectively. Experimental evidence was provided for the case of cubic crystal films,[25] with radiation incident at 26°–34° off normal. Infrared absorption at LO frequencies has also been experimentally demonstrated in thin SiO_2 films by Hubner *et al.*[2] in transmission and by Olsen and Shimura[8] in multiple internal reflection with polarized radiation. In addition, Boyd and Wilson[3] showed that the SH feature

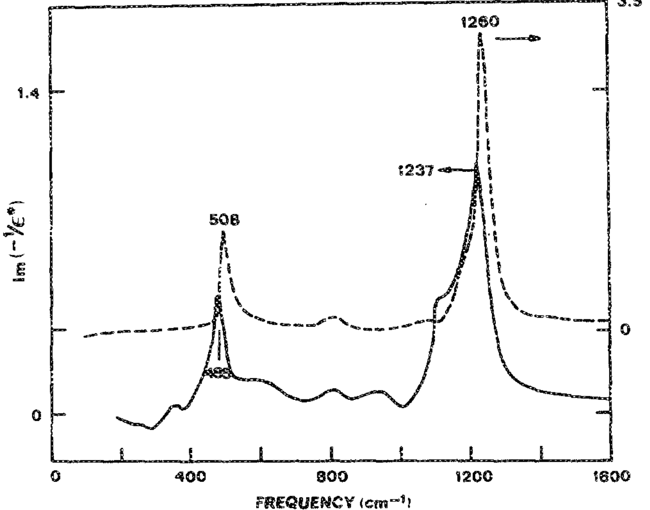

FIG. 7. Energy-loss function (LO spectra) of bulk porous SiO_2 gel (full curve) and bulk v-SiO_2 (dashed curve). (Adapted from Ref. 13.)

completely disappears for SiO_2 films thinner than 18 nm, whereas its intensity gradually increases with thickness for films thicker than 18 nm. These observations support the conclusions of Berreman,[25] since long-range Coulomb interactions are unlikely to be effective along a direction perpendicular to such thin films, thus preventing the observation of the LO mode. As far as the high-frequency dominant band, the samples of Figs. 3–5 differ mostly in the shape of the SH feature and its intensity relative to the TO peak and also, to some extent, the frequency and the full width at half maximum (FWHM) of the TO peak itself. The SH band should not be confused with the LO peak, just as the shoulder in the specular reflectivity spectrum of SiO_2 (Ref. 13) cannot be identified with the pure LO mode. However, the SH frequency falls always in the LO frequency range and the calculations of Philipp[18] showed that the LO peak itself, located at 1260 cm^{-1} for v-SiO_2 and at $\sim$1237 cm^{-1} for a typical bulk, porous SiO_2 gel,[13] clearly evolves from the SH feature located at $\sim$1200 cm^{-1} for bulk v-SiO_2. Those calculations showed that, as the incidence angle for transmission measurements changes from 0° (normal incidence) to 80° off normal, the SH feature sharpens and its intensity and frequency increase, in good agreement with the IR transmission results of Hubner *et al.*[2] at oblique incidence. Assuming that the SH feature is indeed a broadened signature of the LO mode in the transmission spectra, that is, a mixed LO/TO mode of dominant LO character, as suggested by Hu[26], one still has to explain why does this feature show up in all the conventional (normal incidence) transmission measurements, which should only excite the TO absorption component. As a possible explanation, we suggest that maybe there are no pure TO and LO modes in vitreous materials, due to the long range structural disorder effects on the macroscopic electric field produced by long range Coulomb interactions responsible for the TO-LO splittings.[23] In fact, the TO spectra of Fig. 6 appear to have an admixture of the LO spectra of Fig. 7 and vice versa, as revealed in the high-frequency antisymmetric stretching by the shoulders on the high-frequency side of the TO spectra and on the low-frequency side of the LO spectra. Although this effect was more pronounced in the gel spectra, it is perhaps more clearly observed in the simpler spectra of bulk v-SiO_2. In the present absorption spectra, the TO feature near 1070 cm^{-1} is assumed to represent the "true" TO component of the antisymmetric stretch and any changes in the SH feature will be taken as indicative of similar changes in the LO component of the same vibration. It should be pointed out that the SH feature has been alternatively interpreted as also related to an LO mode at $\sim$1160 cm^{-1}, but associated with a TO mode near 1200 cm^{-1}, while keeping the previous assignment for the $\sim$1070 cm^{-1} (TO)–1260 cm^{-1} (LO) pair.[27]

The main changes in the antisymmetric stretching band between the gel films, the gel foil and the thermal oxide relate to (1) the FWHM of the TO peak, (2) the intensity of the SH feature relative to that of the TO peak, and (3) the TO frequency. Next we will discuss each of these points in detail. The FWHM of the TO peak was

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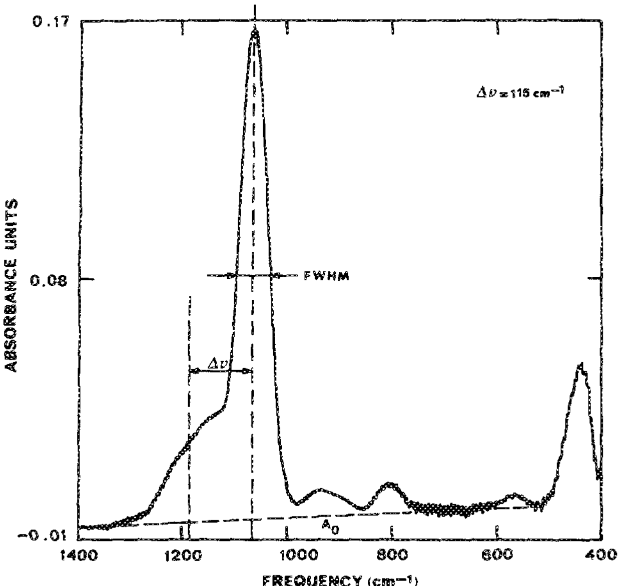

FIG. 8. Graphic procedure for estimating the absorption coefficients of the TO peak and SH shoulder, illustrated for film H_1.

measured as illustrated in Fig. 8 for sample H_1. For the gel foil, the FWHM was taken as twice the width of the low-frequency half of the TO peak. The FWHM was found to vary among the different films, with largest values for the thermal oxide and smallest values for the room temperature dried gels. It varied from 77 cm^{-1} for the thermal oxides, to 65 cm^{-1} for gel films dried at 400–450 °C and 58 cm^{-1} for room temperature dried gel films. The FWHM was 78 cm^{-1} for the gel foil. Although the drying times were not the same for all the samples, these results clearly show a qualitative trend. The central force model[12,28] gives the following expression for the approximate location of the "bare" antisymmetric stretching mode

$$\omega^2 = (k/m_0)(1-\cos\theta) + (4/3)k/m_{Si}, \quad (1)$$

where ω is the angular frequency, k is the Si—O stretching force constant, θ is the average Si—O—Si bridging angle and m_i is the mass of atom i. Although it has been shown that the Si—O distance generally decreases in crystalline silicates when θ increases,[29,30] i.e., the Si—O stretching force constant will increase slightly with θ, we will assume this change to be negligible for small variations in θ. We also assume that any changes in the TO frequency are well approximated by the corresponding frequency changes in the bare mode (without LO-TO splitting), given by Eq. (1). The following equation is thus obtained for the variation in the TO peak frequency with the intertetrahedral angle θ, for a given sample, by differentiation of Eq. (1) with respect to θ

$$\frac{d\omega}{d\theta} = \frac{k\sin\theta}{(2\omega m_0)}. \quad (2)$$

After rearranging, one has the following expression for the spread $\Delta\theta$ in the intertetrahedral angle as a function of the FWHM ($\Delta\nu$) of the TO peak, assuming that the width of the spectral lines is entirely due to the width of a presumable peak in the distribution of angles θ

$$\Delta\theta = \nu\,\Delta\nu/(530.5k\sin\theta) \quad (3)$$

with ν and $\Delta\nu$ in cm^{-1} and k in Nm^{-1}. Although the gel films are expected to have somewhat larger θ and lower k values than the thermal oxide,[13] for the purpose of comparison we will take constant θ and k values at 151° and 569 Nm^{-1}, respectively.[13] Therefore, one finds $\Delta\theta = 24°$ for a typical room temperature dried gel film such as C_0 ($\nu = 1070$ cm^{-1}, $\Delta\nu = 58$ cm^{-1}); for a typical gel film heat treated at 400 °C, such as H_1 ($\nu = 1070$ cm^{-1}, $\Delta\nu = 65$ cm^{-1}), one finds $\Delta\theta = 27°$ and $\Delta\theta = 33°$ for the thermal oxide ($\nu = 1079$ cm^{-1}, $\Delta\nu = 77$ cm^{-1}). These numbers are not meant to be accurate, since $\Delta\theta$ is sensitive to the actual θ and k values. Nevertheless, the above values are in semiquantitative agreement with a spread of the intertetrahedral angle of roughly 60° derived from x-ray radial distribution function studies of v-SiO_2 (Ref. 31) and they indicate that the spread in θ is narrower for a wet porous gel film, presumably because the Si—O—Si bridging sequences are strained near the surface of the gel pores, with larger bridging angles and slightly longer (~ 1%) Si—O bonds, compared to bulk v-SiO_2.[13] The values of the FWHM and $\Delta\theta$ obtained for the thermal oxide are in good agreement with those of Lucovsky *et al.*[14]. However, the ν values were not found to vary significantly with $\Delta\nu$ in the gel films and, when these are compared with the thermal oxide, $\Delta\nu$ is found to increase with ν, instead of decreasing as reported by Lucovsky *et al.*[14] From a structural viewpoint, this is in agreement with the occurrence of strained bonds in the gels, since ν decreases from the thermal oxide to the gels but the simultaneous decrease in $\Delta\theta$ by the effect of strain is stronger and the net result, in terms of Eq. (3), is a decrease in $\Delta\nu$.

The intensity of the SH shoulder is difficult to measure with accuracy. Although a deconvolution of the antisymmetric stretching band could not be done with our instrument software, this procedure would not be very appropriate, given the varying shapes of the shoulders, the complex and variable shapes of the LO peaks (see Fig. 7) and the unknown precise relationship between the SH and LO bands. Therefore, using the following equation to estimate the absorption coefficient α, for a peak absorbance A, with baseline absorbance A_0, for a sample thickness x

$$\alpha = (A - A_0)/x \quad (4)$$

an approximate measure of the ratio of the absorption coefficients at the SH and TO frequencies can be obtained by measuring A for both bands. This was done for TO in each sample at the corresponding TO absorption maximum and for SH at a frequency arbitrarily taken as the TO frequency plus 115 cm^{-1}, which was the approximate difference measured for the gel foil, where the shoulder was best defined (see Fig. 3). The procedure is illustrated in Fig. 8. The absorption coefficient ratios α_{SH}/α_{TO} are given in Table II for a number of different gel films. The absorption ratios clearly decrease with increasing heat treatment temperature.

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TABLE II. Ratio of absorption coefficients for SH and TO vibrational bands of silica gel films.

Film designation[a]	α_{SH}/α_{TO}
$A_t + B_t$	0.15
H_1	0.17
C_0	0.23
F_0	0.42
Gel foil	0.58

[a]For film designation, refer to Table I.

The reason why the SH feature (and consequently the LO) is more intense for porous wet gels than for dry gels and much more intense for the former than for the thermal oxide is now discussed. When bulk porous SiO_2 gels were compared to bulk v-SiO_2, it was found[13] that the frequency of the LO mode for a typical room temperature dried gel ($\sim 1237\ cm^{-1}$) was considerably lower than that of v-SiO_2 ($\sim 1260\ cm^{-1}$), but the LO frequencies cannot be directly extracted from the SH bands of the present spectra. On the other hand, the LO/TO intensity ratio extracted from the data of Figs. 6 and 7 was equal to 0.29 for the room- temperature dried bulk porous SiO_2 gel and 0.24 for bulk v-SiO_2,[13] exhibiting the same trend as the gel films, but with different absolute values, as one might expect given the approximations involved in the present analysis. Porous Vycor also exhibited an enhanced SH feature in the absorption index spectra calculated by Kramers–Kronig analysis of reflectivity.[13] The fact that the SH feature is always more intense for more porous and humid gels than for cured gels or the thermal oxide may tentatively be explained as follows. The presence of SH in the absorption spectra of films, for normal incidence of radiation, may perhaps be due to the imperfectly defined TO and LO characters of the vibrational modes in glasses and amorphous materials in general, leading to an admixture of LO character with the dominant TO response of the absorption spectra as previously argued. However, porous samples will scatter the ~ 10-μm wavelength IR light to some extent (scattering of the shorter wavelength visible light is clearly indicated by the slightly milky appearance of most gels), sending this light in all directions even for normal incidence of the radiation. Therefore, some of the absorbed light will effectively have been obliquely incident, which should make the LO mode (and consequently SH) more clearly visible and therefore more intense than in less porous or dense samples. Such effect is expected to become more pronounced as the porosity increases, in agreement with the present data and with the previous observations for porous Vycor.

Several authors have found interesting correlations between the TO frequency of SiO_2 films and physical properties such as the thickness, for thermal oxide films,[3,4,14] the porosity and strain in electron-beam evaporated films and the thickness and porosity for spin-on films. In the present data, although the TO frequencies of the gel films were slightly lower than in the thermal oxide, the frequency shifts were generally not substantial and this aspect will not be further discussed.

IV. CONCLUSION

A series of spin-on silica gel films have been deposited on c-Si substrates and their structure was characterized. The films were either dried at room temperature or subjected to partial densification near 450 °C.

The refractive indices of the films were lower than that of thermal oxide films by $\sim$0.06–0.03. The FTIR absorption spectra of the gel films showed the presence of residual OH groups, mostly hydrogen bonded, whereas very little molecular water or organic species were left. In the fundamental regime, the main differences between the gel and the thermal oxide spectra consisted in a peak at $\sim$940–960 cm^{-1} due to Si—OH or Si—O^- species in the former, a narrower TO peak at $\sim 1070\ cm^{-1}$ and a more intense shoulder (SH) at $\sim 1200\ cm^{-1}$, all in the gel spectra. The spread in intertetrahedral angles was estimated at $\sim 24°$ and $\sim 27°$, for room temperature dried gels and partially densified films, respectively, compared to 33° for the thermal oxide, confirming a certain degree of strain in the Si—O—Si bridging angles and bonds near the surface of the gel pores. The increasing intensity of the SH feature (from which the LO mode evolves and becomes fully visible, for oblique incidence of the IR light) with decreasing heat treatment temperature may be due to a stronger admixture of LO character into the dominant TO mode in porous gels, which scatter more strongly in all directions the normally incident IR light.

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