SOL–GEL TRANSITION IN SIMPLE SILICATES
III. Structural studies during densification *

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Raman spectroscopy and DSC were used to determine the structure and average heat of formation of siloxane species formed during the gel-to-glass conversion. Based on structural studies of cyclic model compounds and MO calculations of ring strain energies, we conclude that 3 and 4-fold siloxane rings are responsible for the strong Raman bands at 608 and 490 cm^{-1}, respectively.

1. Structural evolution

Two previous papers [1,2] reported on the chemistry, growth and local structure of silicate polymers formed in solution prior to gelation. We now turn our attention to the structure of these same systems during desiccation and subsequent thermal treatments employed for densification.

In sol–gel processes based on metal alkoxide syntheses, the network forms sequentially as a product of condensation reactions. During the initial sol to gel transition, the evolving siloxane network must be stable with respect to hydrolysis. This stable network is reflected in the structure of the desiccated gel (xerogel). However, during the gel to glass conversion, in which the porous xerogel is transformed into a dense glass, condensation reactions continue at temperatures less than T_g where the viscosity is normally in excess of 10^{13} Poises [3]. We show that in this intermediate temperature regime, large concentrations of "energetic" defect species are formed which, due to the very high viscosity, are unable to dissociate to lower energy, stable configurations (until higher temperatures are reached where viscous sintering occurs). In this paper, Raman spectroscopy and differential scanning calorimetry (DSC) are employed to determine the structure and average heat of formation (ΔH_f) of siloxane species formed during the gel to glass conversion. These results are interpreted on the basis of *ab initio* molecular orbital (MO) calculations and structural studies of model compounds.

2. Experimental

2.1. Sample preparation

SiO_2-gels (B2 in ref. 2) were prepared using a two-step hydrolysis procedure employing either water in natural isotopic abundance or ^{18}O enriched water. The first step consisted of hydrolyzing tetraethylorthosilicate (TEOS) with 1 mol. H_2O/Si under acid conditions. The addition of water plus base comprised the second step. The final H_2O/Si mole ratio equalled ~ 4. After gelation at room temperature, the solvent ethanol (or THF) was evaporated at 50°C. In order to eliminate fluorescence in the Raman spectra, most samples were initially heated in air according to the schedule: 1°C/min to 350°C (600 min hold); 1°C/min to 650°C (60 min hold). In several experiments, these gels were then exposed to water vapor (H_2O or H_2 ^{18}O) and reheated as described later.

Cyclic disiloxanes used as model compounds were synthesized by oxidizing di-mesityl di-t-butyl disilene in either air or ^{18}O enriched oxygen following methods developed by West and co-workers [4].

2.2. Methods of analysis

Thermal gravimetric (TG) and DSC measurements were performed under flowing Ar using a DuPont 1090 Thermoanalyzer and Perkin Elmer Model DSC-2 calorimeter, respectively. Specific surface area was determined from the nitrogen adsorption isotherm measured with a Micromeretics Digisorb Model 2600. Raman experiments were performed in flowing helium using the 514.5 nm excitation line of an Ar^+ laser.

3. Results and discussion

3.1. Raman spectroscopy

Fig. 1 shows representative Raman spectra (0–1400 cm^{-1}) of the SiO_2 gel after desiccation at 50°C, after heating to 680°C, and after densification at 1000°C. The broad features of the densified SiO_2 gel spectrum at about 430, 800, 1065 and 1200 cm^{-1} can be explained quantitatively in terms of a central force dynamical calculation applied to a continuous random network model [5]. The sharp features at about 480 cm^{-1} (D_1) and 610 cm^{-1} (D_2) are not explained by this model, and, in bulk v-SiO_2, have been ascribed to "defects" arising from broken bonds [6], surfaces of paracrystalline clusters [7], or small planar rings [8] (fig. 2). Previous investigations [9–12] have shown that a prominent feature of the Raman spectra of porous SiO_2 gels after heat treatments between about 300°C and 900°C is the intense D_2 band. For our samples, this band is absent in the 50°C gel, appears below 350°C and
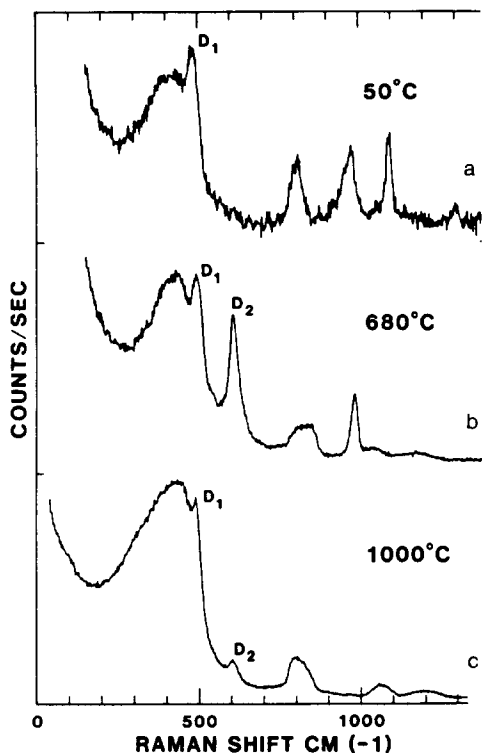
Fig. 1. Raman spectra of SiO_2 gels (a) after desiccation at 50°C, (b) after heating to 680°C according to: 1°C/min to 350°C (10 h hold); 1°C/min to 680°C (1 h hold), (c) after densification at 1000°C.

becomes relatively intense between 600 and 900°C. After gel densification, it is comparable in relative intensity to the corresponding band in conventional v-SiO_2 [12]. We also observe that the D_1 band is quite strong in the 50°C spectrum and that its intensity is less affected by heating than is D_2. Although considerable controversy surrounds a final identification of the origin of these defects, it is generally agreed that their concentrations increase with increasing fictive temperature and with neutron bombardment, and that the vibrations responsible for both D_1 and D_2 involve nearly pure (> 95%) O motion [7].

In a recent investigation of gel structure, we observed that the relative intensity of D_2 increases monotonically, and the relative intensity of a Raman band at 3750 cm^{-1}, assigned to isolated silanols, decreases monotonically in the temperature range 350°C to over 700°C [12]. We proposed that D_2 forms on the gel surface as a condensation product of isolated vicinal silanol groups. If this hypothesis is correct, i.e., if the changing concentrations of isolated silanols and D_2 are not merely coincidental, then condensation reactions between ^{18}O enriched silanols should incorporate ^{18}O into D_2, reducing its vibrational frequency. To achieve this result, a gel (previously heated to 650°C) was exposed to H_2 ^{18}O vapors at 25°C and 100% RH which reduced the relative intensity of D_2 and increased the concentration of silanols in a manner
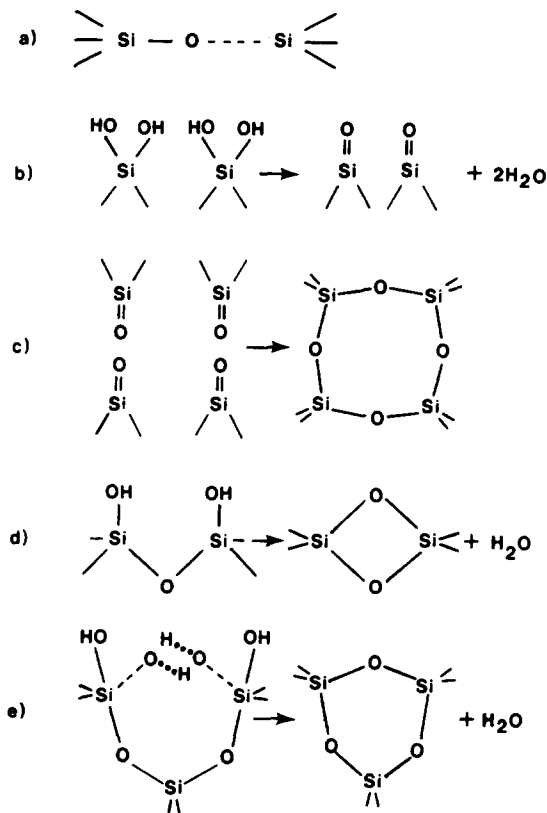
Fig. 2. Defect models for v-SiO$_2$ (a) broken bonds [6], (b) Si = O formation on paracrystalline surfaces (D$_1$) [7], (c) paracrystalline cluster fusion (D$_2$) [7], (d) 2-fold ring formation on a free surface [16] and (e) 3-fold ring formation (surface); dashed lines represent alternate positions for OH in which hydrogen bonding occurs.

previously reported by Krol and Van Lierop [13]. After the relative intensity of D$_2$ had decreased to a level comparable to that in conventional v-SiO$_2$ (24 h), the gel was reheated to 650°C to reform D$_2$. Fig. 3 shows that the frequencies of D$_1$ and D$_2$ are reduced to 486 cm^{-1} and 599 cm^{-1}, respectively, after exposure to H$_2$ ^{18}O and reheating, compared to 493 cm^{-1} and 608 cm^{-1} for a gel exposed to H$_2$O vapor and reheated. This proves that both D$_1$ and D$_2$ form on the gel surface as products of condensation reactions. The narrow bands at 3749 cm^{-1} and 3737 cm^{-1} are assigned to stretching modes of non-hydrogen-bonded vicinal SiO–H and Si^{18}O–H, respectively. The relatively low intensity of the 3737 cm^{-1} band suggests that ^{18}O substitution occurred in only a small proportion (< 20%) of the vicinal SiO–H sites.

Of the numerous models proposed to explain D$_1$ and D$_2$ in bulk v-SiO$_2$, only the small planar ring (SPR) model [7] and (less likely) the paracrystalline cluster interface (PCI) model [7] are consistent with D$_1$ and/or D$_2$ being
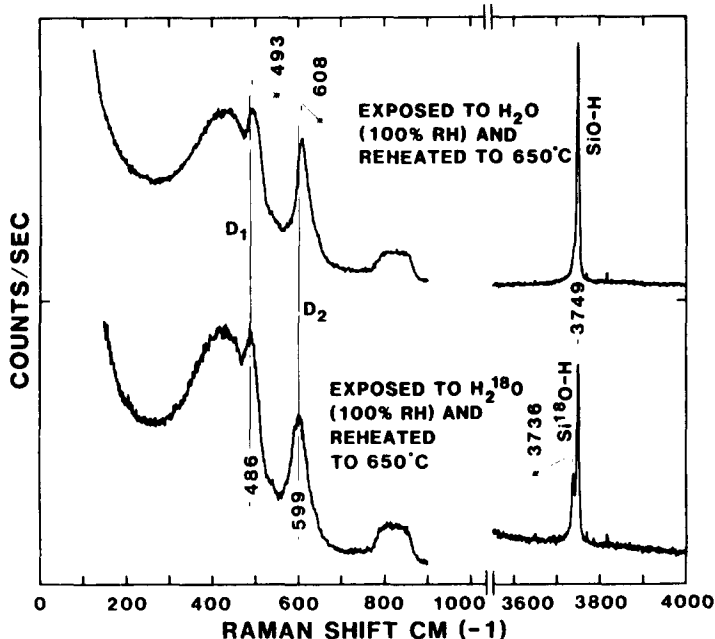
Fig. 3. Raman spectra of SiO_2 gel after an initial heat treatment to 650°C and exposure to (a) H_2O (100% RH) and reheated to 650°C, (b) H_2 ^{18}O (100% RH) and reheated to 650°C.

products of condensation. In the following two sections, we compare both experimental estimates of the heat of formation of siloxane defects and Raman spectra of model compounds to theoretical predictions derived from MO calculations in order to test the validity of these models.

3.2. DSC

In the PCI model, D_1 is assigned to a doubly bonded $Si = O$ species periodically arranged on the [100] surfaces of paracrystalline domains [7]. D_2 tentatively assigned to four-fold rings ($n = 4$ when n equals the number of Si atoms contained in one ring) results from partial cluster fusion. For D_1 to be a product of condensation, the PCI model requires geminal silanols = $Si(OH)_2$ as precursors to D_1 (fig. 2b). D_2 forms subsequently at the expense of D_1 (fig. 2c). In the SPR model, the formation of small planar rings ($2 \leq n \leq 4$) is easily envisioned as resulting from condensation of adjacent silanols on the gel surface as illustrated in figs. 2d and 2e.

Recent MO calculations by O'Keeffe and Gibbs [14] and Kudo and Nagase [15] on model molecules indicate that it should be possible to distinguish between these defect models on the basis of their heats of formation. The heat of formation of 2- and 3-fold rings from unstrained siloxane precursors is calculated to be $+ 55.4$ and $+ 24.4$ kcal/(mol. of rings), respectively [14]. These
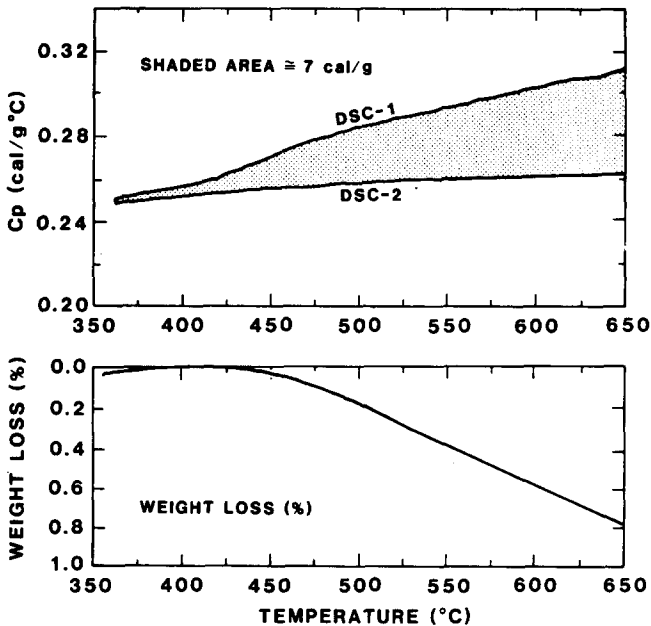
Fig. 4. Weight loss and heat capacity curves (350–650°C) for an SiO_2 gel initially heated to 650°C and exposed to H_2O (100% RH for 24 h). DSC-2 is a repeat scan after cooling from 650°C at 80°C/min.

energies reflect ring strains which result from reducing the Si–O–Si bond angle, θ, from 144° (the most probable θ in v-SiO_2) to approximately 91° and 138°, respectively. The formation of 4-fold rings from the silanone, $H_2Si = 0$, $4H_2Si = O \rightarrow H_8Si_4O_4$, as in the PCI model, is calculated to be 319 kcal/mol., exothermic [14,15].

DSC was used to calculate the average ΔH_f of siloxane bonds in the temperature range 350–650°C where Raman experiments reveal D_2 to be formed [12]. The gel was initially heated to 650°C (so that changes in surface area and skeletal structure would be minimized during the DSC experiment) and exposed to 100% RH for more than 24 h, greatly reducing D_2. Identical samples were then heated under flowing Ar in both the DSC and TGA to reform D_2. Fig. 4 shows weight loss (due to condensation of H_2O) and heat capacity for the SiO_2 gel specimens heated at 20°C/min between 350°C and 650°C after an initial 100 min hold at 350°C to remove physically absorbed water and most hydrogen-bonded hydroxyls. DSC-2 is a repeat scan (after cooling to 350°C at ~ 80°C/min) which represents the heat capacity of the silicate skeleton.

The difference between heat capacity curves (DSC1–DSC2 $\cong$ 7 cal/g_{gel} in fig. 4) represents the sum of the energies due to: (1) the measured loss in surface area, 31 m^2/g, (2) the formation of 4.4×10^{-4} mol. of Si–O–Si/g_{gel} =

$(7.9 \times 10^{-3} \; g_{H_2O}/g_{gel}$ removed $\times 1/18$ mol. H_2O/gH_2O, assuming 1 mol. of Si–O–Si to be formed per mole of water removed), and (3) any structural changes which do not produce water. Assuming a surface energy of 4.8×10^{-2} cal/m^2 for a partially hydroxylated surface, from the DSC results we calculate an average ΔH_f of $+19.3$ kcal/mol. which is close to the strain energy per mole of 3-fold rings. Although we do not know exactly how to partition this energy between the formation of D_1, D_2 and bulk (defect free) silica, corresponding Raman experiments show that the relative intensity of D_2 increases greatly with respect to both D_1 and the broad 430 cm^{-1} band, suggesting that D_2 is the predominant siloxane species formed during these experiments. This endothermic result argues strongly against the PCI model. Since we expect that all of the ring strain energy results from ring closure, the measured value can be interpreted as 19.3 kcal/(mol. of ring closures) which is only slightly less than the strain energy calculated for 3-fold rings and much less than that calculated for 2-fold rings. Therefore, the DSC investigations argue against the PCI model and support Galeener's assignment of D_2 to 3-fold rings [8]. We now present Raman evidence which further supports this assignment.

3.2. Model compound studies

The Raman and DSC results together prove that the species which is the source of the D_2 Raman band is the product of a significantly endothermic reaction involving surface silanol groups. The most likely product of such a reaction is a small, strained siloxane ring. Four-fold and larger siloxane rings are relatively unstrained [16]. Two-fold (cyclic disiloxane) and 3-fold (cyclic trisiloxane) rings are the most likely candidates for the source of the D_2 Raman band. Based on IR studies of a high surface area silica powder (CABOSIL) Michalske and Bunker [16] recently concluded that between 170 and 500°C, the ring structures formed on the surface via dehydroxylation are indistinguishable from more or less strain-free ring structures present in the bulk. They propose that, above 400°C, neighboring silanols which share a common siloxane bridge condense to form 2-fold rings (fig. 2d) and show that these silanols should appear non-hydrogen bonded in the IR spectrum.

The Raman spectra of isolated molecules and cyclosilicate minerals may allow us to distinguish between 2- and 3-fold rings as being responsible for D_2. Cyclic trisiloxane minerals [17] and hexamethyl cyclo-trisiloxane [18,19] show ring breathing modes between 580 cm^{-1} and 654 cm^{-1}, a range which brackets the 608 cm^{-} position of the D_2 Raman band. Galeener et al. [20] have shown that for 3-fold rings, the ring breathing mode is almost completely decoupled from the siloxane network and involves almost pure oxygen motion. This type of mode is consistent with the narrow linewidth of the D_2 Raman band, the absence of a silicon isotope shift for D_2 [17], and the presence of a significant oxygen isotope shift for D_2. Until now the spectra of cyclic disiloxane minerals and molecules are unreported. In this section, we compare the Raman spectra of cyclic disiloxane molecules to the SiO$_2$ gel spectrum and vibrational
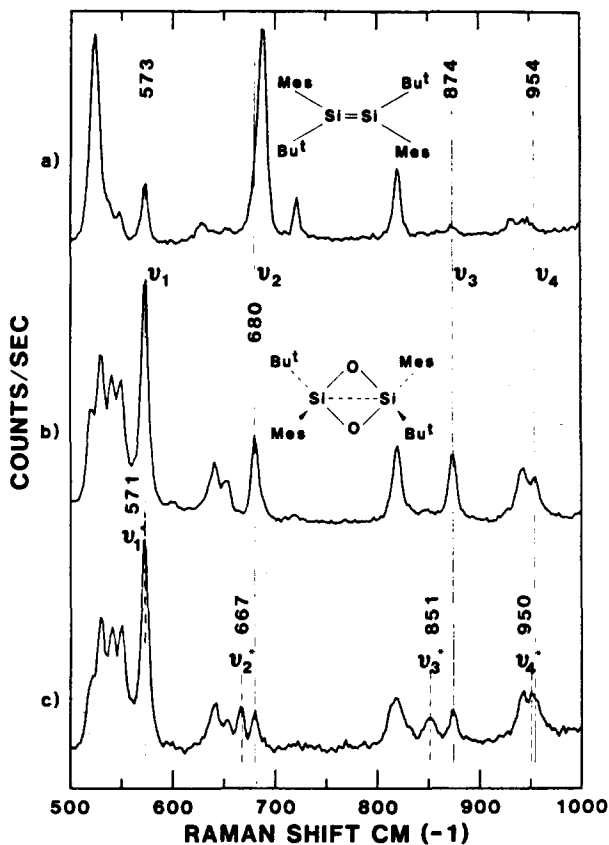
Fig. 5. Raman spectra of (a) di-mes di-t-butyl disilene, (b) compound (a) oxidized in air and (c) compound (a) oxidized in ^{18}O enriched air. ν_1–ν_4 are produced by oxidation. ν_1^*–ν_4^* result from ^{18}O enrichment.

frequencies calculated by Kudo and Nagase for the cyclic molecule, $H_4Si_2O_2$ [15].

In fig. 5 are displayed the Raman spectra of dimesityl di-tert-butyl disilene (a), the cyclic disiloxane product formed by air oxidation (b), and the cyclic disiloxane product formed by oxidation in ^{18}O enriched oxygen (c). The disilene precursor is believed to be slightly oxidized. With air oxidation Raman bands at 573, 680, 874, and 954 cm^{-1} intensify. These Raman bands are believed to correspond to the disiloxane ring modes ν_1 through ν_4 that have been calculated [15] for $H_4Si_2O_2$ (see fig. 6). ** Of these modes, ν_1 and ν_3 involve the least motion of substituents attached to the disiloxane ring and are, therefore, the most likely to occur in a cyclic disiloxane residing in a silica

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** These calculations normally result in an overestimate ($\leq 10\%$) of the vibrational frequency [14]; for example, ν_1 and ν_3 (a$_g$ symmetry) are observed at 94.4% of the calculated frequency.
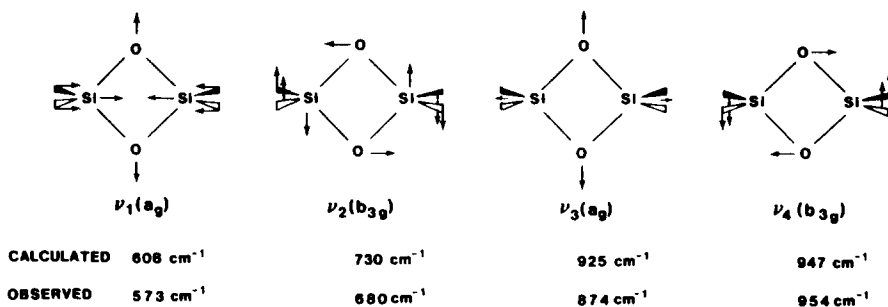
Fig. 6. Raman-allowed vibrations calculated for $H_4Si_2O_2$ [15] along with frequencies observed in di-mes di-t-butyl disiloxane.

matrix. While the Raman band corresponding to ν_1 occurs near D_2, the ν_1 band shows negligible oxygen isotope effect and must involve predominantly silicon motion, as predicted [15] by theory. In contrast, D_2 in a highly ^{18}O enriched SiO_2 gel synthesized in an aprotic solvent is shifted by 30 cm^{-1} (to 580 cm^{-1}) proving that the D_2 vibration involves nearly pure oxygen motion. ν_3 shows a large oxygen isotope effect; however, ν_3 occurs at too high a frequency to correspond to D_2 in SiO_2. Therefore, the model cyclic disiloxane compound produces no Raman bands which reasonably correlate to D_2, and we conclude D_2 results from 3-fold rings.

If the 3-fold siloxane ring is associated with the D_2 Raman band, then it is reasonable to associate the lower frequency D_1 Raman band, which is present during gelation and is relatively unaffected by water vapor, with the relatively unstrained [16] 4-fold (cyclic tetrasiloxane) ring. The Raman spectrum of octamethyl cyclo-tetrasiloxane [19] supports this hypothesis, since it includes a siloxane ring mode at 480 cm^{-1} near the position of the D_1 Raman band at 493 cm^{-1}.

4. Conclusions

We have shown that in the temperature range 350–650°C, D_1 and D_2 form on the gel surface as products of condensation reactions involving primarily isolated vicinal silanols. Based on the average ΔH_f of siloxane bonds (350–650°C) and Raman investigations of cyclic disiloxane model molecules, we exclude the PCI model and 2-fold rings as explanations for D_2. Our DSC and Raman results are consistent with Galeener's assignment of D_2 to 3-fold rings [9]. Raman studies of 3-fold cyclosilicate minerals [17] and model compounds show ring breathing frequencies in the range 580–654 cm^{-1} which are consistent with D_2 in the SiO_2 gel spectrum. D_1 is stable during gelation and is relatively unaffected by water vapor. Thus, Galeener's assignment of D_1 to the breathing vibration of a 4-fold ring is consistent with both our results and Raman spectra of isolated molecules [8,17,18]. We conclude that, although

it is possible for adjacent silanols (which subsequently condense to form 3- and 4-fold rings) to be hydrogen bonded [16], prior to ring closure these silanols are sufficiently separated to appear isolated in the Raman spectrum (fig. 2).

Heat treatments which reduce the viscosity below $\sim 10^{13}$ P allow reformation of the silica surface greatly reducing the concentration of strained species (D_2).

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