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Raman scattering from pristine and oxidized polysilanes

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The polymer backbone, as well as the Si-H vibrational, modes of polysilanes $(\text{SiH})_n$ and $(\text{SiH}_2)_n$ have been identified through Raman scattering techniques. The intensities of these modes were then studied as a function of the oxidation of the sample. With time, one can see the growth of certain modes which can be identified as those arising from SiHO, SiH_2O , and SiH_2O_2 groupings. The relationship between the stretching and bending modes of these clusters is discussed and compared to those existing in amorphous silicon hydrogen ($a\text{-SiH}_x$). A further comparison is made with a study on the sample kept in an oxygen-free atmosphere.

I. INTRODUCTION

There exists a considerable amount of interest in polymers and amorphous materials. In particular, a fundamental understanding of amorphous silicon ($a\text{-Si}$) and its hydrogen derivatives ($a\text{-SiH}_x$) is of special interest due to their technological importance.¹ Two related compounds, SiH_4 and $(\text{SiH}_2)_n$, which exist in the form of polymers, have been prepared only recently.² These materials, the structures of which are shown schematically in Fig. 1, are intrinsically interesting as new polymers, and, in addition, may provide input for understanding the vibrational spectra of $a\text{-SiH}_x$ which also contains groupings of SiH and SiH₂ clusters.

The eigenvectors and eigenfrequencies of the vibrational excitations of these clusters in $a\text{-SiH}_x$ have been calculated

by Brodsky *et al.*³ and Lucovsky *et al.*⁴ and have also recently been the subject of an extended review article by Cardona.⁵ The modes which have been observed in $a\text{-SiH}_x$ and which should be present in polysilanes as Si-H

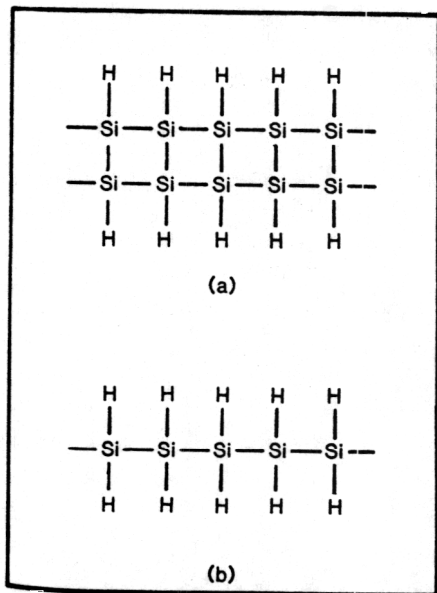


FIG. 1. Schematic representations of the polymers (a) $(\text{SiH})_n$ and (b) $(\text{SiH}_2)_n$.

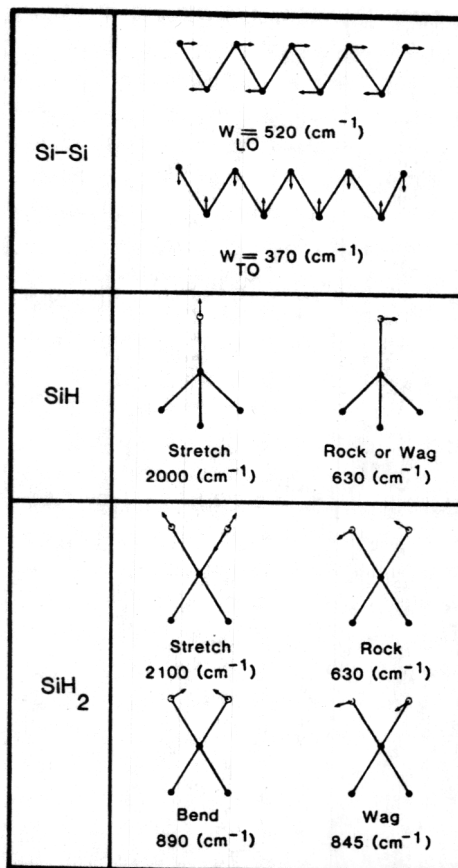


FIG. 2. Si-Si and Si-H vibrational modes observed in amorphous SiH_x (from Refs. 4 and 6). Closed circles (●) and open circles (○) represent Si and H, respectively.

rocking, bending, and stretching modes are shown in Fig. 2.⁴ These modes have been observed mostly by infrared spectroscopy. Raman spectroscopy is complementary to IR and so provides additional information on these modes, especially those at low frequency ($<400\text{ cm}^{-1}$) which are more difficult to access with IR techniques. It has been noted that the frequencies attributed to the cluster modes of silicon-hydrogen compounds vary by as much as $\sim 25\text{ cm}^{-1}$ depending on the method of preparation in the case of $\alpha\text{-SiH}_x$ films and also on the detection technique (Raman or IR) used.³ In this paper, we will compare and contrast the results of previous spectroscopic studies of materials containing SiH_x clusters with our Raman measurements of polysilanes. We will also consider theoretical calculations predicting the frequencies for such molecular clusters.

For the polysilanes, our Raman scattering work provides the first information on the low-lying Si-Si backbone modes for the polymers. There have been theoretical calculations⁶ predicting these modes using central-force models (i.e., ignoring Si-H interactions). Polysilane $(\text{SiH}_2)_n$ promises to be a better candidate for the comparison of such model calculations to experiment than say polyethylene $(\text{CH}_2)_n$, where the C-C bond distance is shorter than the former, implying a large interference due to the hydrogen atoms. We have observed the low-frequency modes of $(\text{SiH}_2)_n$ and again a comparison is made with corresponding modes in $\alpha\text{-SiH}_x$ and theory.

Another, and perhaps a more relevant motivation for this article, is to acquire a better grasp on the aging properties of $(\text{SiH}_2)_n$ and $(\text{SiH})_n$ polymers. As is the case for $\alpha\text{-SiH}_x$, polysilane reacts strongly with oxygen through the breaking of Si-Si bonds.⁷ This leads to an increase in the intensities of the Raman scattering peaks corresponding to the vibrational frequencies of the SiH_2O_2 and also SiHO clusters. In addition, there may be evidence for the growth of an SiH_2O band as well. This paper also gives the results of a systematic study on the growth of such clusters. A consistency comparison is also made with corresponding modes in $\alpha\text{-SiH}_x$.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Polysilane was prepared through the reduction of dichlorosilane, SiH_2Cl_2 with granular lithium.² A rust-colored powdery solid was deposited and was shown by chemical analysis to be mostly $(\text{SiH}_2)_n$. IR spectra of the samples² studied showed the expected characteristic doublet assigned to the bending and rocking modes of the polysilane chain.⁴ After preparation, samples were loaded into glass tubes in an inert-atmosphere glove box. The tubes were capped and sealed by applying epoxy to a ground-glass joint. After shipment from Edinburgh to East Lansing, samples were reloaded into O-ring-sealed glass tubes in an inert-atmosphere glove box with less than 0.5 ppm O_2 . A period of about one and one-half months elapsed between the initial sample preparation and the Raman measurements. As will be seen in the following discussion it appears that the samples were somewhat unstable against slow decomposition from pure $(\text{SiH}_2)_n$ to a

mixture of $(\text{SiH}_2)_n$ and $(\text{SiH})_n$.

For the convenience of Raman scattering studies the powder was pressed into a pellet and held in a vertical position in a glass tube sealed with paraffin-wax film. Slow oxidation of the sample took place via atmospheric leakage through the film.

An argon-ion laser provided the incident beam ($\lambda_0=4880\text{ \AA}$) for the scattering studies. The power of the beam was measured as $\sim 30\text{ mW}$ at the sample. A Jarrell-Ash double-grating monochromator was used for the analysis of the scattered light. Alignment of the sample consisted of focusing a line image of the beam on the pellet surface, thereby minimizing the power density to which the sample was exposed. The scattered light was collected and focused on the spectrometer slit in the back-scattering 90° geometry arrangement. The incident beam was horizontally polarized in the scattering plane to maximize the coupling of the incident light into the sample. A measurement of the depolarization spectrum⁸ of the sample did not yield meaningful results, probably due to the intense parasitic scattering associated with the granular quality of the sample.

All scans were taken with the sample at room temperature but local temperatures due to the incident-beam heating could have been $\approx 30^\circ\text{C}$. Owing to the large fluorescent emission of the sample, an initial time of $\approx 2\text{ h}$ was allowed for the quenching of the background before Raman spectra were acquired. In order to obtain meaningful results for relative intensity comparisons, utmost care was taken to not disturb the scattering arrangement for the entire duration of the experiment.

III. RESULTS AND DISCUSSION

A. Polysilane spectra

A typical Raman-spectrum scan from the polysilane sample is shown in Fig. 3. This particular scan is the initial scan of the sample before the onset of oxidation. In spite of the fluorescence emission on which the Raman spectrum is superposed, four relatively broad peaks can be clearly seen. These frequencies can be approximately estimated to be at energy transfers of 482, 630, 900, and 2115 cm^{-1} . The errors for these bands are estimated to be at $\pm 5\text{ cm}^{-1}$.

The dominant mode at 482 cm^{-1} can be clearly attributed to Si-Si chain backbone vibrations as shown in Fig. 2. According to theoretical calculations⁶ using a central-force model, $(\text{SiH}_2)_n$ should exhibit two optical modes with calculated frequencies at

$$\omega_{\text{TO}} = (4\alpha_{\text{Si-Si}}/m)^{1/2}$$

and

$$\omega_{\text{LO}} = \sqrt{2}\omega_{\text{TO}},$$

where m ($46.9 \times 10^{-24}\text{ g}$) is the mass of a Si atom and $\alpha_{\text{Si-Si}}$ ($1.7 \times 10^5\text{ dyn cm}^{-1}$) is the Si-Si central-force constant.⁹ After substitution of the above specified values of the mass and force constant into Eqs. (1) and (2) one obtains the values $\omega_{\text{TO}}=370\text{ cm}^{-1}$ and $\omega_{\text{LO}}=520\text{ cm}^{-1}$.

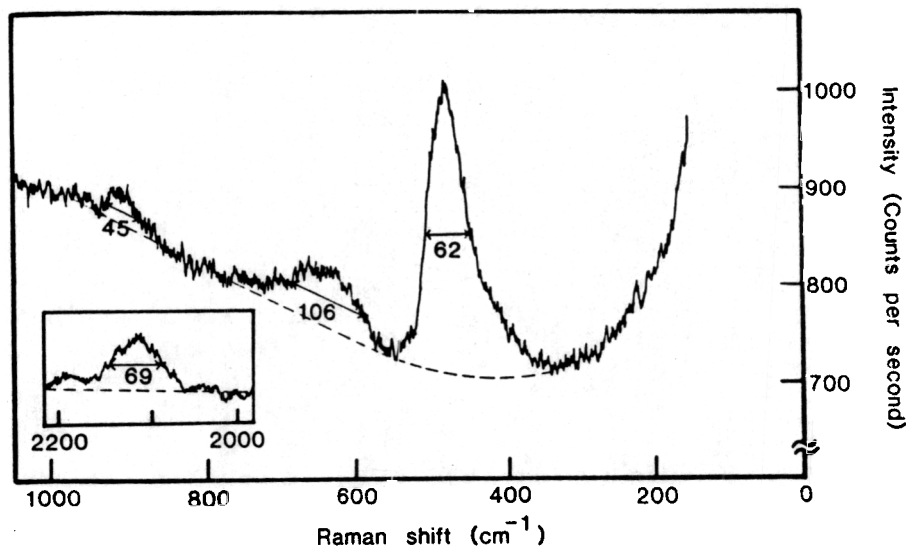


FIG. 3. Typical Raman scattering scan of the polysilanes. Peaks have been identified and are discussed in the text and correspond to the Si-Si backbone (480 cm^{-1}), Si-H rocking ($\sim 630\text{ cm}^{-1}$), bending ($\sim 909\text{ cm}^{-1}$), and stretching ($\sim 2115\text{ cm}^{-1}$) modes. The widths of the peaks in cm^{-1} are also indicated. Note that the abscissa in this figure and those which follow is linear in wavelength rather than wave number. Dashed line in this spectrum and following spectra represents the luminescence background.

The observed 480-cm^{-1} ($\Delta\nu \sim 62\text{ cm}^{-1}$) peak is clearly the Si-Si mode. The difference between the observed and calculated values is probably due to the simplicity of the model which ignores hydrogen-silicon interactions as well as the disorder associated with the finite polymer length. There were clear indications in some of the recorded Raman spectra of a lower-frequency peak existing at $\sim 260\text{ cm}^{-1}$, as can be seen from Fig. 4. However, this mode could not be consistently observed in all samples and occurred only in initial samples with very little oxidation. This mode is probably equivalent to the 210-cm^{-1} mode observed in *c*-Si as well as in some *a*-Si samples.⁵ The nonobservance of this mode in our partially oxidized samples is consistent with the fact that its intensity is expected to be low⁵ and is a manifestation of the subtle changes of

the local Si-Si order. Silicon-silicon modes at 380 and 480 cm^{-1} were also seen in the Raman spectra of hydrogenated amorphous silicon by Brodsky *et al.*,³ but the 380-cm^{-1} peak is very weak and is observed only in samples with low hydrogen concentration ($\leq 10\text{ mol \% H}_2$).

The other three polysilane modes which we observe at 630 , 909 , and 2115 cm^{-1} can be attributed to the SiH₂ rocking, bending, and stretching modes, respectively. The frequencies corresponding to these modes for Si-H molecular groups have been determined from observed measurements on hydrogenated amorphous silicon.^{3,4} The results and mode assignments for SiH, SiH₂, and clusters deduced from these infrared studies are shown in Fig. 2 as noted earlier. For the SiH₂ groups, Lucovsky *et al.*⁴ assign values of 630 , 890 , and 2100 cm^{-1} to the rocking, bending, and stretching modes. These values are very close to our observed values of 630 , 909 , and 2115 cm^{-1} for polysilane. Lucovsky *et al.*⁴ also observe an additional peak at $\sim 845\text{ cm}^{-1}$, close to the 890-cm^{-1} bending mode. This lower-frequency peak has been explained as being due to symmetry splitting of the 890-cm^{-1} mode if neighboring SiH₂ groups form segments of the polymer (SiH₂)_n. This doublet is very well resolved in the IR absorption spectra of our samples,² but the low-frequency component was not observed in the corresponding Raman spectra. Our failure to observe the 845-cm^{-1} component can be attributed in part to the large intrinsic width of this peak ($\Delta\nu \sim 45\text{ cm}^{-1}$) and to a small peak-to-background ratio caused by the large fluorescence background, but is primarily a reflection of the weak Raman activity which this lower-frequency component is expected to exhibit.⁵ The discrepancy of $\sim 20\text{ cm}^{-1}$ in the observed frequencies of the bending mode (our 909 cm^{-1} vs 890 cm^{-1} as seen by Lucovsky *et al.*⁴) may be attributed to the difference in the configuration of an SiH₂ cluster in polysilane versus

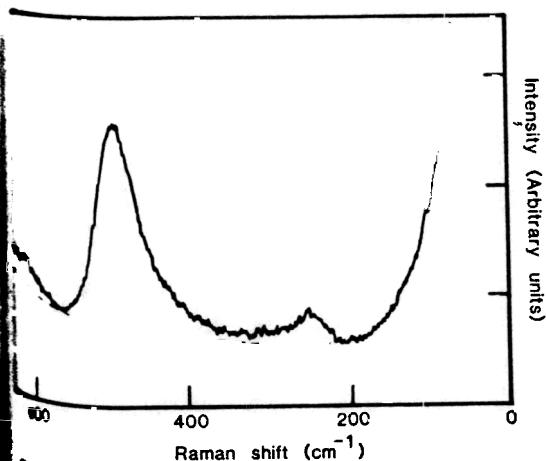


FIG. 4. Scan showing the low-frequency $\sim 260\text{-cm}^{-1}$ mode.

that in α -SiH_x. In particular, the bending-mode frequency in question depends on the H—Si—H and H—Si—Si bond-bending force constants, respectively. From symmetry considerations the latter should be the same in polysilane and α -SiH_x, whereas an increase in the former due to a slight reduction in the H—Si—H bond angle in (SiH₂)_n could account for the 20-cm⁻¹ upshift. The IR study² of our sample yielded a bending mode frequency at 907 cm⁻¹ which is consistent with the Raman result and in good agreement with the assignment of this mode as the bend of SiH₂ which is both Raman and IR active.

The observed frequency of the Si—H stretch (~2115 cm⁻¹) is also consistent with the presence of SiH₂ clusters in our sample. From the observance of this peak alone, however, it is difficult to rule out the possibility of the existence of SiH₃ clusters. The observed width of this peak ($\Delta\bar{\nu}_4 \sim 69$ cm⁻¹) incorporates the Si—H stretching frequency for SiH₃ clusters expected at 2140 cm⁻¹. Nevertheless, SiH₃ clusters should also give rise to a second doublet expected at 862 and 907 cm⁻¹, the lower-energy component of which was not seen in either IR or Raman scans taken on the sample.²

It is possible to do a consistency check on the hydrogen content of the sample as demonstrated by Brodsky *et al.*³ If α represents the number of hydrogen atoms per silicon atom in the sample and N equals the number of silicon atoms, then the ratio of the intensities of a single Si—H stretching mode (I_{2115}) and the Si—Si LO mode (I_{480}) could be written as

$$\frac{I_{2115}}{I_{480}} = \frac{N_{\text{Si-H}}}{N_{\text{Si-Si}}} \frac{\sigma_{\text{Si-H stretch}}}{\sigma_{\text{Si-Si stretch}}} \quad (3)$$

or

$$\frac{I_{2115}}{I_{480}} = \frac{\alpha}{2-\alpha/2} \frac{\sigma_{\text{Si-H stretch}}}{\sigma_{\text{Si-Si stretch}}} \quad (4)$$

where $N_{\text{Si-H}}$ is the number of single Si—H bonds, $N_{\text{Si-Si}}$ is the number of Si—Si bonds, $\sigma_{\text{Si-H stretch}}$ is the cross section of Si—H stretch, and $\sigma_{\text{Si-Si stretch}}$ is the cross section of Si—Si stretch. The ratio of the cross sections can be approximated from the measurements of Bethe and Wilson¹⁰ of the Raman spectrum of disilane (Si₂H₆) liquid. From the scans taken by these authors, the observed inten-

sity of the Si—H stretch mode is 1.9 times that of the Si—Si stretching mode. But since there are six single Si—H bonds in a single disilane molecule, the scattering cross section of a single Si—H bond is 1.9/6, ~0.32 times that of the Si—Si stretch (Brodsky *et al.* estimate this value to be 0.4 instead). Using our estimated value for the ratio of cross sections and substituting this in Eq. (4) (see Table I for our initial observed I_{2115}/I_{480} value to be ~0.37), we obtain a value of $\alpha = 1.5$. This implies that our sample has a hydrogen content lower than the expected value of $\alpha = 2$.

It is possible that in addition to spontaneous decomposition of (SiH₂)_n into an admixture of (SiH₂)_n and (SiH)_n, the local heating of the sample due to the laser beam causes cross linking, thus contributing to the production of a mixture of (SiH₂)_n and (SiH)_n clusters in the sample. Further evidence of the existence of (SiH)_n comes from the oxidation studies (see Sec. III B). In fact, a simple estimate can be made of the ratio of (SiH₂)_n clusters as compared to (SiH)_n clusters. If N_1 is the number of Si atoms in SiH clusters and N_2 is the number of Si atoms in SiH₂ clusters then the total number of single Si—H bonds equals $N_1 + 2N_2$. This can be equated to αN , the total number of single Si—H bonds in the sample. Also, we know that $N_1 + N_2 = N$, the total number of Si atoms. Thus $N_2 = N(\alpha - 1)$ and for $\alpha = 1.5$, one obtains $N_1 = N_2 = N/2$. So this simple analysis indicates that the sample contains equal amounts of SiH and SiH₂ clusters. However, a SiH stretching frequency expected at 2000 cm⁻¹ for such clusters was clearly not resolved in our scans. It is likely that the surroundings of such clusters has shifted this band to a higher frequency,^{11,12} thereby masking it in the low-energy tail of the 2115-cm⁻¹ stretching mode of the SiH₂ cluster. Also, note that the intensity of the 2000-cm⁻¹ peak should be approximately half of that of the 2115-cm⁻¹ peak assuming equal numbers of SiH and SiH₂ clusters and identical scattering cross sections for the Si—H stretch in both clusters. The only other mode generated by a SiH cluster is a wagging mode at 630 cm⁻¹ which is accidentally degenerate with and therefore indistinguishable from, the 630 cm⁻¹ rocking mode of SiH₂ clusters.

As a final point in the discussion of the spectrum of polysilane we note that the low value of α deduced above implies a very low probability for the existence of SiH clusters in our samples. Indeed, no evidence for such clusters [e.g., the dominant stretching mode at 2140 cm⁻¹ (Ref. 4)] was found in our spectra.

B. Oxidation

The change in the Raman spectra of polysilane as a function of time (or oxidation) is shown in Fig. 5. Table I also gives the absolute intensities of the four peaks as oxidation takes place. Within the experimental widths of the peaks (see Fig. 3), there was no appreciable change in the peak positions.

As a function of time, the fluorescence emission of the sample increases dramatically and after 7 d it is so intense relative to the Raman signals that there is a gross error introduced in the measurement of Raman intensity. There

TABLE I. Intensity dependence of several Raman bands in the spectra of polysilanes as a function of time (exposure to oxygen). Intensities in counts per second are measured as the peak amplitude above the (estimated) luminescence background.

Day	I_{480}	I_{630}	I_{907}	I_{2115}
0	300	55	30	110
	265	40	40	140
	340	80	70	220
	440	60	too weak to detect above background	250
4	390	80	100	325
7	500	100	125	400
8	450	75	~125	2450

FIG. 5. Raman spectra of polysilane as a function of time (or oxidation) is shown in Fig. 5. Table I also gives the absolute intensities of the four peaks as oxidation takes place. Within the experimental widths of the peaks (see Fig. 3), there was no appreciable change in the peak positions. As a function of time, the fluorescence emission of the sample increases dramatically and after 7 d it is so intense relative to the Raman signals that there is a gross error introduced in the measurement of Raman intensity. There

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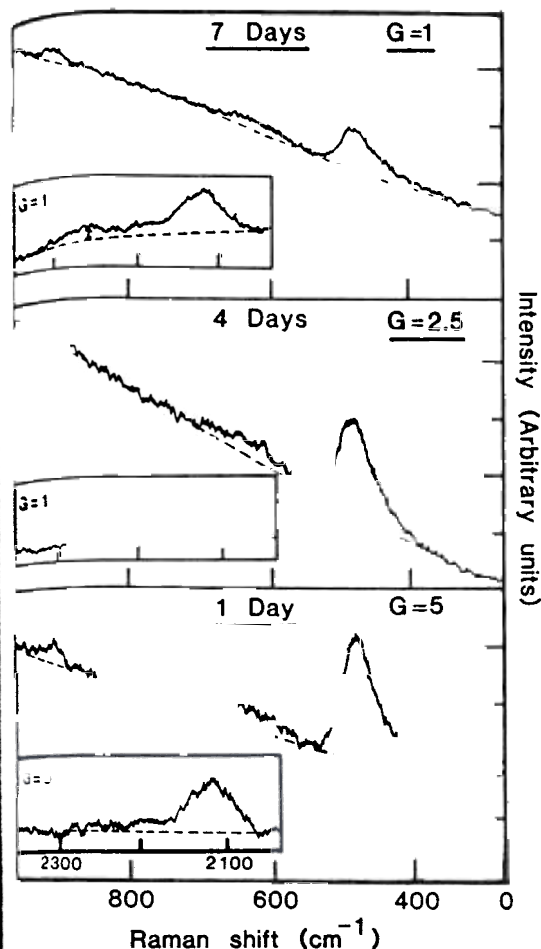


FIG. 5. Evolution of the Raman spectra of the polysilanes as a function of oxidation. Owing to increased fluorescence the peaks have been plotted on different scales (or different gains, G).

we do not include for analysis Raman data acquired after 8 d of exposure. With increased oxidation, the sample gradually changes color from orange to white. These observations are consistent with the breaking of Si-Si bonds. We would therefore expect a decrease in the intensity of the Si-Si, 482-cm⁻¹ stretch mode. Experimentally however, we see an increase in the intensity I_{482} by 50% during an interval of 8 d. A similar increase was also seen in the Si-H rocking intensity I_{630} . This absolute increase is an artifact of the increase in the Raman scattering sampling volume,¹³ which is associated with the increase in the optical gap,² and a corresponding decrease in absorption at the wavelength of both the incident and scattering photons.

There are more dramatic and real increases in the intensities of the Si-H bending mode I_{909} and the Si-H stretching mode I_{2115} with oxidation. These dramatic increases are necessitated by the increased fluorescence.

However, the values of the absolute intensities given in

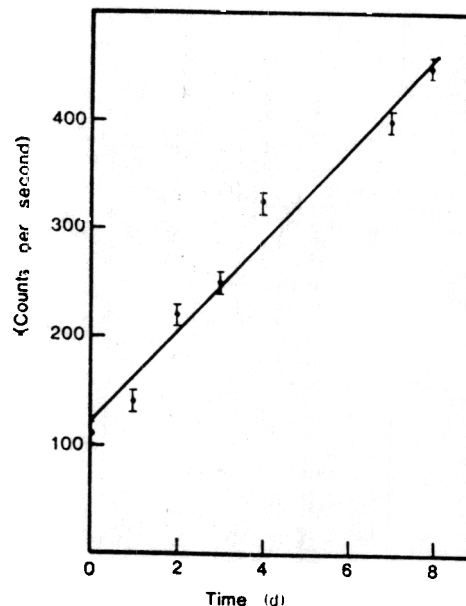


FIG. 6. Time dependence of the intensity of the peak at 2115 cm⁻¹. Solid line is a linear least-squares fit to the data points.

Table I clearly show these changes. The intensities of both the 2115- and 909-cm⁻¹ peaks increase approximately by a factor of 4 during a period of 8 d.

A plot of the absolute intensity I_{2115} as a function of time (or oxidation) is shown in Fig. 6. The points with some scatter generally fall on a straight line. It has been shown⁷ that the SiH stretching mode in a SiHO cluster exists at 2090 cm⁻¹. As argued in the preceding section, our sample possibly contains local (SiH)_n clusters. Breaking of the Si-Si bonds and the recombination to oxygen produces local SiHO clusters. Since the width of the original SiH line at 2115 cm⁻¹ is ~69 cm⁻¹, the downshift due to oxidation to 2090 cm⁻¹ is not well resolved. The growth of SiHO clusters thus contributes to the intensity of the SiH stretching peak. The dramatic increase in the intensity of this peak indicates a higher scattering cross section with oxidation. Growth of the corresponding IR absorption line due to oxidation of α -SiH_x (Ref. 7) has also been observed.

The reaction of oxygen with the (SiH₂)_n clusters is likely to produce SiH₂O and eventually SiH₂O₂ clusters. The SiH stretching frequencies in these clusters are expected to be at 2180 and 2240 cm⁻¹, respectively.³ The growth of the latter however is not as dramatic as that of the 2115-cm⁻¹ mode but is observable at 2250 cm⁻¹ after approximately 4 d of oxidation (see Fig. 5). The 2250-cm⁻¹ peak is sufficiently broad so that it may contain an unresolved contribution from the ~2180-cm⁻¹ SiH₂O mode. The growth of intensity of the SiHO cluster peak starts to saturate after the 2250-cm⁻¹ SiH₂O₂ peak begins to appear. If SiH and SiH₂ clusters are present in equal amounts as indicated previously then the preferential growth of the bands associated with oxidation of SiH clusters in comparison with the sluggish growth of those associated with

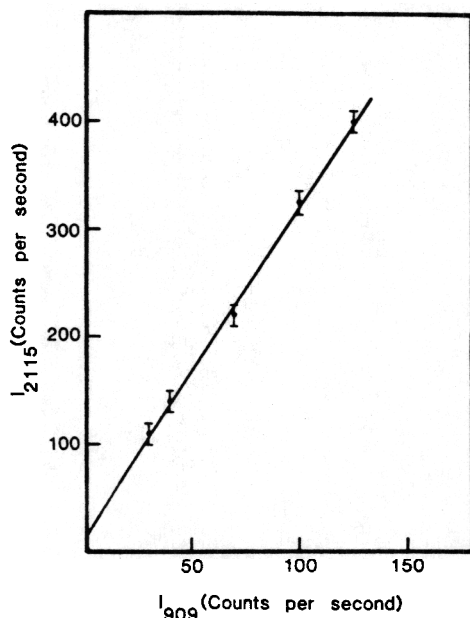


FIG. 7. Relationship between the intensities of the 2115- cm^{-1} and 909- cm^{-1} peaks. Solid line is a linear least-squares fit to the data.

SiH_2 clusters suggests that Si-Si bonds in the former are considerably weaker than those in the latter.

The ratio of the growth with oxidation of I_{2115} to that of I_{909} is plotted in Fig. 7. The straight-line nature of the plot is clear evidence that the modes giving I_{2115} and I_{909} are related but the relationship is much more subtle than that between the SiH bending and stretching modes in $\alpha\text{-SiH}_x$,¹¹ for example.

As noted, since the broad SiH stretch at 2115 cm^{-1} overlaps the Si-H stretch in O-Si-H, the two excitations must have different Raman cross sections; otherwise one would detect no change in the 2115- cm^{-1} intensity with oxidation. Now the bending mode at 909 cm^{-1} is derived from an SiH_2 cluster but these clusters react at a much slower rate with oxygen than do the SiH clusters as noted above. Therefore the growth of the 909- cm^{-1} mode is not, in fact, a growth in the intensity of the SiH_2 bending mode with oxidation, but rather, it must arise from some other excitation that occurs at a similar frequency. The obvious candidate for such an excitation is an Si-O vibration which has been observed in $\alpha\text{-SiH}_x$ in the (800-1000)- cm^{-1} region.⁷

The analysis presented in the preceding paragraph can be simply expressed in precise mathematical terms and shown to be consistent with all of the features exhibited in Figs. 6 and 7.

Let N_1 = the number of SiH clusters, N_2 = the number of SiH_2 clusters, and n = the number of O-Si-H bonds. We then specify the relevant Raman cross sections as follows: σ_S is a cross section for an Si-H stretch in an SiH or SiH_2 cluster, σ'_S is a cross section for an Si-H stretch in an O-Si-H cluster, σ_B is a cross section for an SiH₂ bend at 909 cm^{-1} , and $\sigma_{\text{Si-O}}$ is a cross section for an

Si-O stretch at $\approx 909 \text{ cm}^{-1}$. Then if we assume that the observed Raman intensity of a given vibration is identically equal to the product of the cross section and the number of clusters generating that vibration (i.e., set intervening constants equal to 1),

$$I_{2115} = 2N_2\sigma_S + (N_1 - n)\sigma_S + n\sigma'_S, \quad (5)$$

or, for $n = at$ where $a = \text{constant}$ and $t = \text{time}$,

$$I_{2115} = a(\sigma'_S - \sigma_S)t + (2N_2 + N_1)\sigma_S. \quad (6)$$

Similarly,

$$I_{909} = a\sigma_{\text{Si-O}}t = N_2\sigma_B. \quad (7)$$

By elimination of the term " at " from Eqs. (6) and (7) one finds that

$$I_{2115} = \left[\frac{\sigma'_S - \sigma_S}{\sigma_{\text{Si-O}}} \right] I_{909} + \left[(2N_2 + N_1)\sigma_S - N_2 \frac{\sigma_B}{\sigma_{\text{Si-O}}} (\sigma'_S - \sigma_S) \right]. \quad (8)$$

Equation (6) accounts for the linear behavior and positive-ordinate intercept shown in Fig. 6. Moreover, the positive slope I_{2115} vs t indicates that $\sigma'_S > \sigma_S$ as expected. The linear behavior and positive intercept seen in the plot of I_{2115} vs I_{909} (Fig. 7) is in agreement with the behavior predicted by Eq. (8). In particular, since, from Eq. (6) and Table I, $I_{2115}(t=0) = (2N_2 + N_1)\sigma_S = 110 \text{ counts/sec}$, and from Eq. (7) and Table I, $I_{909}(t=0) = N_2\sigma_B = 3 \text{ counts/sec}$ and $\sigma'_S - \sigma_S / \sigma_{\text{Si-O}} = 3.07$ (see Fig. 7), we calculate the intercept of I_{2115} vs I_{909} to be +18 counts/sec, in good agreement with the observed value of 18 counts/sec. This positive intercept is a manifestation of

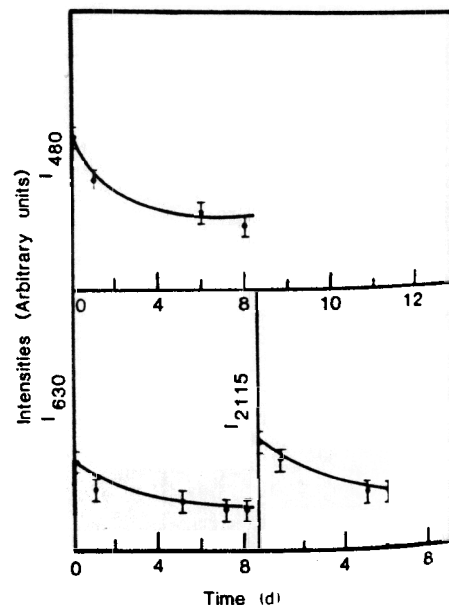


FIG. 8. Time dependence of the Raman spectrum of a certain sample (see text for discussion).

fact that SiH_2 groups contribute intensity at both 909 and 2115 cm^{-1} .

C. Sealed sample

The time dependence of the Raman spectra of samples which were maintained in an oxygen-free atmosphere was monitored for comparison with the above-described oxidation studies. Figure 8 shows the behavior of the intensities of the Si-H stretching and wagging modes and of the Si-Si modes. Even with the power of the laser beam as low as 30 mW, the samples show a general but gradual deterioration with time such that all intensities fall to approximately half their value after 8 d of laser illumination. It is also clear that the time dependence of the observed intensities is quite different in the case of the oxidized and unoxidized samples.

Thus the apparent photostructural effects exhibited by the unoxidized sample are probably present in the time-dependent studies of the oxidized samples as well but constitute a minor contribution to the intensity changes which are observed.

IV. SUMMARY AND CONCLUSIONS

A mixture of $(\text{SiH}_2)_n$ and $(\text{SiH})_n$ polymers has been prepared with and without the exposure to oxygen. The vibrational excitations associated with the Si-Si backbone

and also those corresponding to the Si-H stretching, bending, and wagging modes have been identified and discussed. Comparisons and contrasts have been made with the IR scans taken on these samples as well as those on hydrogenated amorphous silicon.

The oxidation study consisted of the observance of the changes in the vibration spectra of the polymers. It was observed that the scattering cross section of the Si-H stretch in SiH or SiH_2 clusters is lower than in the SiHO cluster. The growth of these clusters correlates well with the appearance of the vibration frequency corresponding to the Si-O stretching mode. Also, the oxidation of the $(\text{SiH})_n$ appears to occur more rapidly than the oxidation of $(\text{SiH}_2)_n$. These assertions are supported by quantitative consistency arguments which account for the changes in specific features of the Raman spectra of polysilanes with oxidation.

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