Chem. Mater. 1994, 6, 977–982 977

Infrared Spectroscopic Study of Thin Films of Poly(methylsilane), Its Oxidation, and Its Transformation into Poly(carbosilane) on the Surfaces of Silicon Single-Crystal Wafers

Mihai Scarlete, Stéphane Brienne, Ian S. Butler,* and John F. Harrod*

Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 2K6

Received February 18, 1994. Revised Manuscript Received April 20, 1994⊗

The use of pol(methylsilane) (PMS) as a pyrolytic precursor to thin layers of silicon carbide (SiC) on silicon single-crystal wafers has been examined. The enhanced IR signals resulting from the multiple internal reflections that occur within the thin layers deposited on the chemically polished Si surfaces have been used to monitor the oxidation and pyrolysis of PMS. The complex phenomena involved in the Kumada transformation of PMS into a poly(carbosilane) layer have been investigated in the 100–450 °C range. The oxygen content of the starting polymer has a pronounced effect on the resulting vibrational spectra. The data indicate that the Kumada rearrangement for PMS takes place at ~200 °C, i.e., at a much lower temperature than was reported previously.

Introduction

Crystalline, microcrystalline, and amorphous silicon carbide (SiC) films are now widely used in advanced semiconductor technology, e.g., these films are the preferred material for today's hetero-emitter junction bipolar transistors[1] and the windows in *p-i-n* amorphous silicon solar cells,[2] amorphous SiC LED or electrophotographic receptors.[3] The utility of SiC is due to two intrinsic characteristics. Firstly, SiC has a wider band gap than does Si, thereby facilitating the production of high power devices that operate at high temperatures, its use as a spectroscopic window material and as a built-in potential barrier for carriers induced by the photovoltaic effect in high-performance solar cells. Secondly, the superior chemical stability of SiC films is important in their use in integrated circuits for smart sensors.

Pyrolysis of poly(carbosilane) (PCS) has been used to prepare SiC films for the windows in *p-i-n* amorphous silicon solar cells.[4] Also, relatively pure bulk SiC can be obtained from the pyrolysis of PMS at temperatures below 1000 °C.[5] The Kumada rearrangement[6] of PMS to PCS, which apparently occurs at ~400 °C, the decomposition of PCS to hydrogenated SiC, and the subsequent formation of β-SiC have been monitored by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of the bulk material. The PMS used in the earlier pyrolysis studies, however, exhibited a considerable degree of oxidation—the average formula of the material employed was $Si_1C_{0.9}H_{<0.2}O_{0.1}$, which implies ~4 wt % oxygen (this fact was suggested to be the main reason why the fibers did not exhibit the high-temperature strength and stability expected for pure SiC).[5] The DRIFTS data reported in the literature[5] are for a mixture of PMS and polysiloxanes. The potential of PMS in the electronics industry as a SiC-layer precursor is ultimately dependent on the production of extremely pure SiC, with only an oxygen level in the ppm range being acceptable. A recent elemental analysis of carefully synthesized and pyrolyzed polysilylethylene revealed an oxygen content in the 0.22–6.65 wt % range.[7]

The measurement of accurate oxygen levels in these types of material is difficult. Infrared spectroscopy is the most convenient analytical method for the ppm range, because of the high absorption coefficient of the Si–O–Si antisymmetric stretch which is observed as a strong and broad band in the 1100–1000-cm^{-1} region. To our knowledge, the oxygen content during the earlier work on the pyrolysis of PMS was never reduced to the level required for electronic processing.[8] The vibrational modes of the siloxane groups complicate the IR spectrum, especially in the Si–H stretching (2100–2000 cm^{-1}) and 1100–1000 cm^{-1} regions. The methylene wagging mode at ~1050 cm^{-1} is obscured. This peak, together with a peak at 1352 cm^{-1}, are important fingerprints for PCS formation.[9]

In the present work, silicon single-crystal wafers with a surface orientation [100] have been used as supports for thin layers of PMS, as well as those of PCS and SiC, which are subsequently produced by pyrolysis. The silicon single-crystal wafers served as the window material for the transmission IR measurements in the 4000–600 cm^{-1} range. The reflecting properties of the chemically polished wafers

---

⊗ Abstract published in *Advance ACS Abstracts*, June 1, 1994.

(1) Sasaki, K; Fukazawa, T.; Furukawa, S. Proceedings of International Electron Devices Meeting, Washington, D. C. *Tech. Dig.* **1987**, 186.

(2) Tawada, Y.; Kondo, M.; Okamoto, H.; Hamakawa, Y. *Sol. Energy Mater.* **1982**, *6*, 299.

(3) Bujalski, R. J. European Patent Application 200326, 1986.

(4) Chu, C.-J.; Ting, S.-J; Mackenzie, J. D. Amorphous and Crystalline Silicon Carbide III, Proceedings of the 3rd International Conference; Howard University, Washington D. C. In *SPP* **1990**, *56*, 87.

(5) Zhang, Z. F.; Babonneau, F.; Laine, R. M.; Mu, Y.; Harrod, J. F.; Rahn, J. A. *J. Am. Ceram. Soc.* **1991**, *74*, 670.

(6) (a) Shiina, K.; Kumada, M. *J. Org. Chem.* **1958**, 23, 139. (b) E. Hengge In Silicon Chemistry II, 51; *Top. Curr. Chem.* **1974**, 43.

(7) Corriu, R. J. P.; Leclerc, D.; Mutin, P. H.; Planeix, J. M.; Vioux, A. *Organometallics* **1993**, *12*, 454.

(8) Laine, R. M.; Babonneau, F. *Chem. Mater.* **1993**, *5*, 260.

(9) The CH_2 deformation (scissors) mode at 1351 cm^{-1} is much weaker than is the CH_2 wagging mode at ~1050 cm^{-1}. For example, on comparing the IR spectra of hexamethyldisilane, $(CH_3)_3Si–Si(CH_3)_3$, and bis(trimethylsilyl)methane, $(CH_3)_3Si–CH_2–Si(CH_3)_3$, the fingerprint vibration for the CH_2 group is the 1058-cm^{-1} band, while the 1351-cm^{-1} band is not observed at all.

0897-4756/94/2806-0977$04.50/0

Table 1. Infrared Spectrum of PMS

obsd IR bands (cm^{-1})	vibrational assignments[12,13]
2956 s	$\nu(C{-}H)_{antisym}$
2894 m	$\nu(C{-}H)_{sym}$
2075 s, br,[6] 2120[7]	$\nu(Si{-}H)$
1406 m	$\delta(Si{-}CH_3)_{antisym}$
1247 s,[6] 1260[7]	$\delta(Si{-}CH_3)_{sym}$
930 m	γSiH_2
865 vs	ρCH_3
764 s, br	$\nu(Si{-}C)_{antisym}$
685 s or 650 s	$\nu(Si{-}C)_{sym}$

proved to be especially beneficial in the multiple reflection IR measurements. Another advantage of using silicon as a support for the thin SiC layers obtained by pyrolysis of polysilane precursors may be the possible buffering effect of the surface, for example, in accepting the excess silicon atoms that usually result from the pyrolysis of PMS, or in compensating for the carbon excess found after the pyrolysis of polydimethylsilane.[10]

Experimental Section

Poly(methylsilane) was prepared by a literature method.[12] Briefly, CH_3SiHCl_2 (1 equiv) was refluxed with metallic sodium (2.05–2.10 equiv) in 6:1 hexanes/THF under UHP argon. The terminal Cl groups were removed by subsequently treating the reaction mixture with $LiAlH_4$ at −78 °C for 30 min. The reaction could be readily followed by monitoring the disappearance of the Si(Cl)–H resonance in the ^1H NMR spectrum at ~5 ppm. After reaction, solvents were pumped off and the viscous liquid polymer was redissolved in pure toluene. Following filtration to remove inorganic components, the polymethylsilane was recovered by evaporating the solvent.

To observe the influence of different degrees of oxidation of the polymer on the resulting IR spectra, samples of the polymer were subjected to kinetically restricted oxidation between two KBr or Czochralski (Cz) silicon windows. The KBr windows were sealed with epoxy resin and a special Teflon cell was designed for the silicon windows, provided with inlet/outlet for the oxidizing gas, a mixture of N_2 and air. The substrates were 12–20 Ω cm, n-type doped with phosphorus and [100] orientation. The thicknesses of the layers were measured by means of a Sloan-Dektak profilometer and were in the range of 1 μm. All oxidations were performed at room temperature.

The pyrolyses were performed in a Lindberg single-zone programmable furnace equipped with a Eurotherm PID temperature controller working up to 1100 °C and providing an accuracy of ±1 °C at 1000 °C. The rate of heating was 8 °C/min. Samples were thin films supported on silicon wafers placed directly into the furnace tube. The IR spectra were obtained by multiple reflections from the silicon surfaces resulting in sufficient enhancement of the signals in the deposited layers to be able to record the reflected beams after 64 scans. The spectra (4 cm^{-1}) were recorded on a Bruker IFS-48 spectrometer equipped with an IR microscope, DTGS detector, and a SONY Trinitron PVM 1340 color monitor.

Results and Discussion

Infrared Spectral Analysis of the Oxidation of PMS. Vibrational assignments have been proposed previously for the IR spectrum of PMS (Table 1). The transmission IR spectrum of the polymer used in the present work is shown in Figure 1a. The integrated intensity of the antisymmetric Si–O–Si stretching absorption at ~1100 cm^{-1} was used in estimating the oxygen content of this starting polymer. The calibration procedure was based on the absorption of the interstitial oxygen (Figure 1b) in the supporting silicon wafers which had a concentration of 15 ppma (7.5 × 10^{17} at/cm^3). The oxygen content of the initial PMS polymer was 25 ± 10 ppma.

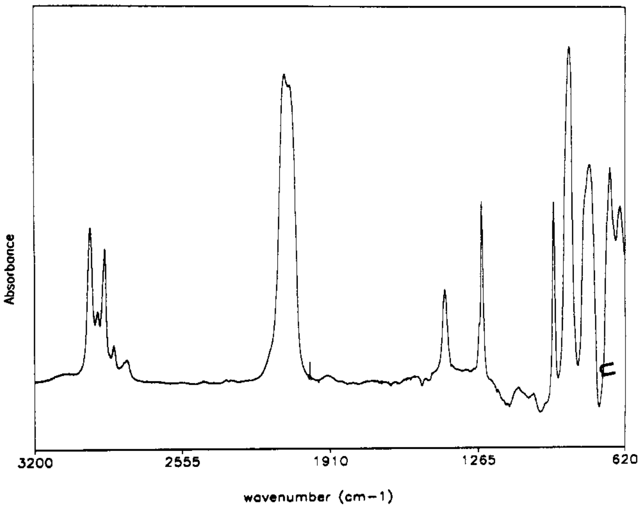

Figure 1. Infrared spectra of PMS.

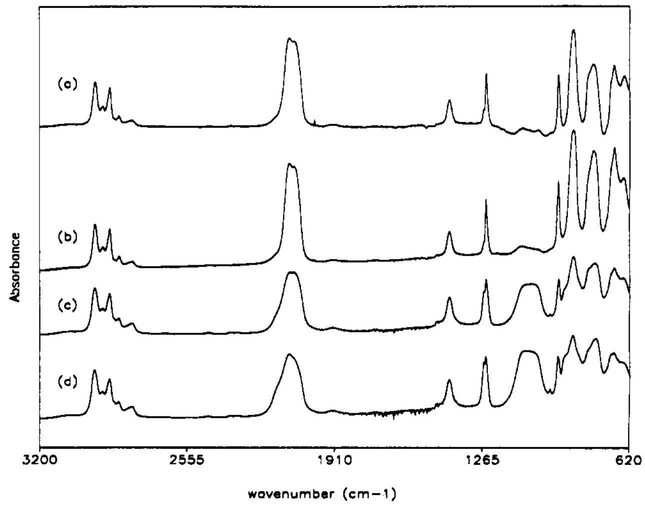

Figure 2. Infrared spectra of PMS during oxidation at room temperature: (a) 1 min; (b) 5 min; (c) 10 min; (d) 20 min; (e) 30 min).

An investigation of the oxidation of PMS revealed several interesting features in the IR spectra: (1) increased intensity of the Si–O stretch accompanied by a corresponding decrease in the intensity of the Si–H stretching band; (2) appearance of a complex structure for the Si–H stretching band; (3) a shift in the symmetric C–H deformation of the methyl group; (4) an anomalous intensity ratio of the symmetric/antisymmetric stretches of the methyl group; (5) separation of the methylene wagging from the Si–O stretch.

A series of IR spectra of a PMS sample supported on a silicon single-crystal wafer during oxidation at room temperature is presented in Figure 2. The most evident change is the increasing intensity of the Si–O–Si antisymmetric stretch at ~1100 cm^{-1}. The change in intensity of this band, expressed as the function $(I_\infty - I_t)$, were I_∞ is the intensity of the peak after complete oxidation and I_t is the intensity of the peak at time t, versus time obeys the parabolic rate law $dI/dt = k/I$ with a correlation coefficient $r = 0.999\,49$. This indicates a diffusion-

---

[10] Hasegawa, Y.; Okamura, K. *J. Mater. Sci.* **1983**, *18*, 3633.

[11] Mu, Y.; Harrod, J. F.; Laine, R. M. *J. Appl. Organomet. Chem.* in press.

[12] Mu, Y. Ph.D. Thesis, McGill University, Montreal, Quebec, Canada, 1991.

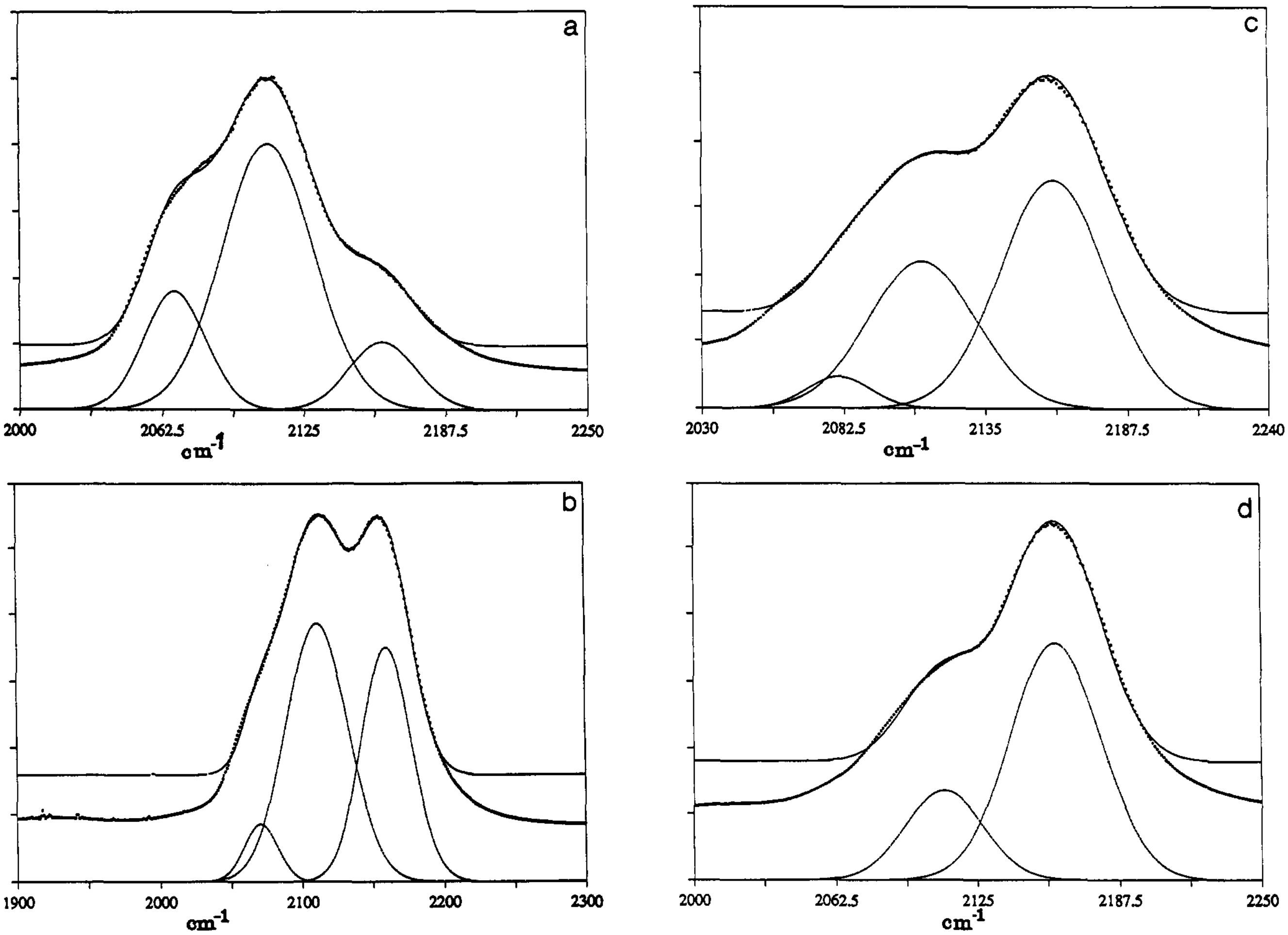

Figure 3. Subband structure of the Si–H stretch at different oxidation times at room-temperature peak-fit procedure: (a) 1 min; (b) 2 min; (c) 8 min; (d) 60 min).

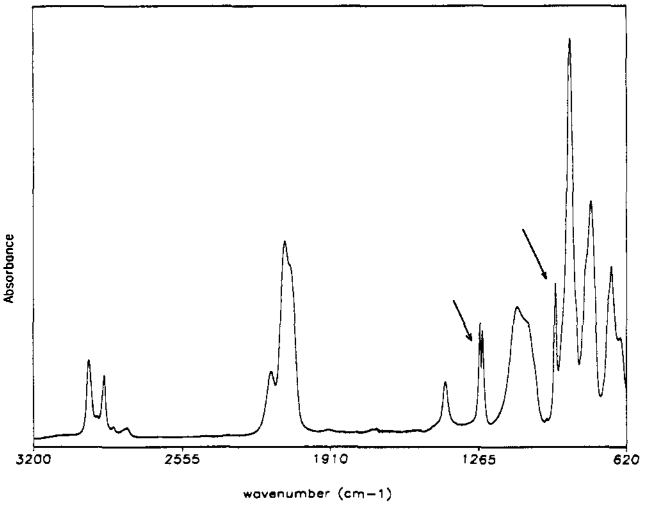

Figure 4. Infrared spectrum (2-cm^{-1} resolution) exhibiting two peaks for the Si–CH_3 deformation at 1248 and 1260 cm^{-1}.

Table 2. Relative Areas of the Peaks following Deconvolution of the Si–H Stretching Band during Oxidation at Room Temperature

total oxidation time before the IR spectrum was recorded (min)	new peak positions (cm^{-1}) (percent area of original peak)		
1	2067 (20.3)	2109 (67.3)	2160 (12.4)
2	2067 (6.9)	2109 (53.7)	2160 (39.4)
8	2079 (4.7)	2110 (36.4)	2160 (58.9)
30	not detected	2110 (24.6)	2160 (75.4)

controlled oxidation process through the siloxane layer (Figure 3).

Another important observation is the broadness of the Si–H stretching band. This band clearly consists of overlapping peaks. A peakfitting procedure (Peakfit), based on the assumption of 100% Gaussian overlapping curves, indicated the presence of three different peaks (Figure 4). The positions of the peaks and their percentage of the total peak area are given in Table 2. The 2160-cm^{-1} band increases in intensity with the degree of oxidation and can be assigned to the Si–H stretch of a silicon attached to an oxygen atom, in agreement with the increased force constant found in siloxanes (the Si–H stretch is located at 2127 cm^{-1} in 1,1,3,3-tetraethyldisiloxane and at 2109 cm^{-1} in 1,1,3,3-tetraisopropyldisiloxane). The 2067-cm^{-1} band can be assigned to the backbone Si–H stretch of PMS. The 2110 cm^{-1} peak is attributed to stretching of the terminal SiH_2 groups of the polymer, while the 928 cm^{-1} peak is associated with the scissors vibration of the SiH_2 groups.

The 2067-cm^{-1} peak disappears completely after the fourth deconvolution cycle. This is accompanied by saturation of the band assigned to the antisymmetric Si–O stretch. At this stage, all the S–Si–H vibrations have apparently been transformed into O–Si–H vibrations. The total decrease in the intensity of the overlapped Si–H peak, taking into account the fact that the terminal SiH_2 groups seem not to be affected (from the constant intensity of the peak at 928 cm^{-1}), is due to the decreased absorption

Table 3. Ratio of the Integrated Intensities of the Symmetric and Antisymmetric C–H Stretches of the Methyl Groups

total oxidation time before the IR spectrum was recorded	peak position (cm^{-1})				
	2067 I_{rel}	2109 I_{rel}	2160 I_{rel}	1048–1095 actual area/final area (%)	2894/2960 ratio
1	11.2	37.0	6.82	67.5	0.94
5	4.58	35.5	26.0	89.9	0.78
10	2.68	20.8	33.6	95.6	0.71
60	not detected	13.3	40.7	100.0	0.56

Table 4. Integrated Areas of the Si–H and Si–O Stretches during the Room-Temperature Oxidation of PMS

	oxidation time (min)			
	1	5	10	60
Si–H stretch intensity	77.5	58.3	50.8	49.2
Si–O stretch intensity	48.6	57.1	50.8	81.8

coefficient (A_0) of the 2160-cm^{-1} peak relative to that of the 2067-cm^{-1} peak (A_1). The ratio of the absorption coefficients of the two vibrational modes ($\ln A_0/\ln A_1$) is 0.78. The Si–H stretch originally located at 2067 cm^{-1} shifts towards higher energies during oxidation possibly because of a long-range delocalization of the electrons in the polysilane backbone. The intensity and position of a Si–H stretch when the Si atom is attached to another Si as in PMS, to O as in the oxidized polymer, to H as in a terminal SiH_2 group, or to C as in PCS is also related to other electronic parameters such as the electron-withdrawing properties of the substituent groups.

Advancing oxidation is reflected in the area of the Si–O peak (percentage of the final area of the peak), while the degree of oxidation can be obtained from the ratio of the adjusted areas of the peaks at 2067 and 2160 cm^{-1}. At the same time, the ratio of the intensities of the symmetric and antisymmetric C–H stretches of the methyl groups is strongly influenced by the oxidation of PMS. These values, which are listed in Table 3, have been normalized with respect to the intensity of the antisymmetric C–H stretch of the methyl group (the integration was performed over the 2995–2938-cm^{-1} range). The resulting integrated areas of the antisymmetric C–H stretch for the PMS sample during oxidation were 7.84, 8.15, 8.29, and 7.87, respectively. If saturation of the Si–O stretch band means total transformation into polysiloxane, then the lowest observed ratio of the intensities of the two C–H stretching vibrations of the methyl group (0.56) should correspond to that observed in polysiloxanes. In the IR spectrum of 1,1,3,3-tetramethylsiloxane, the ratio observed is 0.25. The values observed for higher homologues increase with increasing molecular weight and reach a limit of 0.41 for silicone grease. The integrated areas of the Si–O and Si–H stretches in a series of spectra recorded during oxidation of PMS are given in Table 4. The intensity of the Si–H band decreases as the oxidation proceeds.

The use of the intensity of the Si–H peak as a measure of the degree of oxidation is not straightforward. For instance, its diminished intensity may result from a decreased bond dipole moment due to the electron-withdrawing effect I_- of oxygen (the partial negative charge on hydrogen may be decreased because of the high polarizability of silicon which transmits the I_- effect to hydrogen). Electromeric effects can also interfere in a complicated manner. An empirical, but quantitative, relationship has been established between the intensity (A) of the Ge–H stretch and the Taft–Hammett σ constants of the substituents on Ge in a series of germanium compounds.[13] There is a similar relationship for silicon compounds:[14] $\Delta A^{1/2} = 1.47\Sigma\sigma_p + 0.12$. If the Taft–Hammett σ_p constants in this expression are replaced by the electronegativities of oxygen and silicon, the predicted decrease in intensity at the end of the oxidation process is 0.84, a value which is in reasonable agreement with that of 0.78 obtained from the IR spectra.

During oxidation, the symmetric methyl deformation mode shifts towards higher energies, as does the Si–H stretch. The band goes from 1248 to 1260 cm^{-1} following insertion of oxygen into the silicon backbone. Such an effect on a partially oxidized sample depicting well-separated peaks (resolution 2 cm^{-1}) is shown in Figure 5. Despite the shift to 1260 cm^{-1} observed during oxidation, the peak intensity remained more or less constant. The integrated peak areas (1283–1218-cm^{-1} region) in the four samples were 14.1, 15.7, 14.9, and 14.8, respectively.

The significantly decreased ratio of the intensities of the symmetric and antisymmetric C–H stretches of the methyl groups can also be related to electronic effects. A change in the effective charge on the Ge atom due to the effect of alkyl substituents has already been mentioned in relation to the intensity of the Ge–H absorption.[14] Methyl groups have an I_+ effect. In addition, they seem to participate in the σ–σ conjugation. The sensitivity of the symmetric C–H stretch of the CH_3 groups to the third substituent on the Si atom could then be similarly attributed to restricted conjugation in the polymer backbone. When restricted conjugation occurs, the normal ratio of the two stretching modes is observed (Table 1). Similar changes in the intensities of certain peaks in Ge compounds are also considered to be extremely sensitive indicators of conjugation.[15] The change in the ratio of the intensities of the two methyl group stretches seems to be related to the atom located at the end of the H–C–Si–X chain (X could be Si, O or C in the polymer, the oxidized polymer, or PCS, respectively). The participation of the σ electrons in the C–H bond in an extended σ–σ hyperconjugation in such a chain, based on the significant polarizability of silicon and enhancement of the σ/π-conjugation effect with the difference in donor–acceptor properties of conjugating bonds, has already been detected by spectroscopic methods.[16–19]

Effect of Oxidation on PMS after Heat Treatment at 150–450 °C. The pyrolytically induced transformation of PMS into PCS (previously reported[2] to occur at ~400 °C) involves insertion of a silylene group into a C–H bond. The final product has methylene groups located between the silicon atoms forming the backbone of the polymer. During oxidation, the direct insertion of an oxygen atom

---

(13) Ichikawa, H.; Machino, F.; Teranishi, H.; Ishikawa, T. In Silicon-Based Polymer Science. *Adv. Chem. Ser. No. 224*, **1990**, 619.

(14) Egorochkin, A. N.; Khorshev, S. Y.; Ostasheva, N. S.; Sevasyanova, E. I.; Satge, J.; Riviere, P.; Barrau, J. *J.Organomet.Chem.* **1976**, *105*, 311.

(15) Shambayaty, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 697.

(16) Egorochkin, A. N.; Khorshev, S. Y.; Ostasheva, N. S.; Voronkov, M. G.; Vyazankin, N. S.; Kashik, T. V.; Kuz'min, O. V.; Nametkin, N. S.; Pritula, N. A. *J.Organomet.Chem.* **1975**, *99*, 47.

(17) Egorochkin, A. N.; Viazankin, N. S.; Pritula, N. A.; Chernysheva, T. I.; Spiridonova, G. K. *Dokl. Akad. Nauk. SSSR* **1971**, *1999*, 352.

(18) Khorshev, S. Y.; Viazankin, N. S.; Chernysheva, T. I.; Kashik, T. V. *Dokl. Akad. Nauk. SSSR* **1972**, *2015*, 4.

(19) Egorochkin, A. N.; Viazankin, N. S.; Khorshev, S. Y. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 2074.

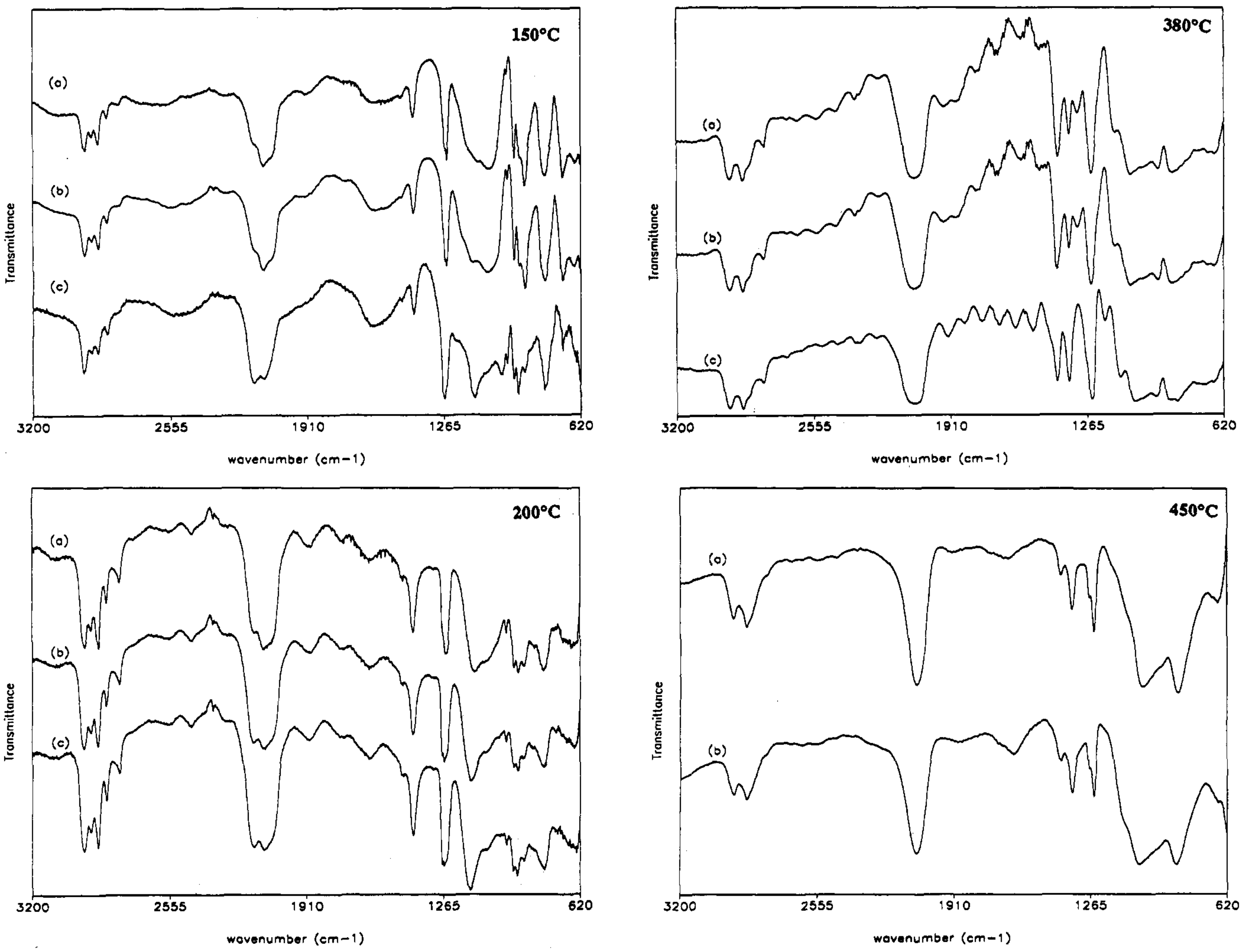

Figure 5. Infrared spectrum of PMS following oxidation at room temperature (after heating for 1 h under inert atmosphere at four different temperatures): (A) 150 °C after (a) 1, (b) 2, and (c) 4 min; (B) 200 °C after (a) 1, (b) 5, and (c) 10 min; (C) 380 °C after (a) 1, (b) 2, and (c) 4 min; (D) 450 °C after (a) 1 min and (b) 2 h.

into the Si–Si bond could be detected spectroscopically. The earlier pyrolysis studies employed a starting polymer with a much higher degree of oxidation. The spectra of the pyrolyzed material exhibited features due to both the polysilane and polysiloxane. The vibrational peaks particularly affected were the symmetric C–H stretch of the methyl group, the wagging vibration of the CH_2 group at 1050 cm^{-1}, and the symmetric deformation of the $Si–CH_3$ group at 1248 cm^{-1}. All three bands are shifted or overlapped in the spectra of polysiloxane. The room-temperature reactivity towards oxygen of samples previously heated in an inert atmosphere (Ar or N_2) at different temperatures in the 150–450 °C range is illustrated by the IR spectra in Figure 5. As a general rule, the same spectral features appear as in the case of oxidation of unheated PMS, but on a different time scale—the higher the preheat temperature in an inert atmosphere, the slower the rate of oxidation at room temperature. Also, specific behavior to the annealed PMS are exhibited. After 1 h at 200 °C, the intensity ratio of the two methyl stretches becomes less sensitive to oxidation. A new and unexpected feature is the sharpening of the 1104-cm^{-1} peak (the Si–O band in methyl-substituted siloxanes has an upper limit of just below 1100 cm^{-1}), a frequency characteristic of interstitial oxygen trapped in a silicon single crystal. The upward shift of the Si–O stretch is characteristic of a highly ordered environment. During oxidation of SiC single crystals, the Si–O stretch shifts to 1100–1088 cm^{-1}, while for the polycrystalline material it is observed at 1094–1086 cm^{-1}.[19]

The IR spectra of PMS samples heated at 300–450 °C in N_2 and subsequently oxidized at room temperature exhibit bands due to both the Si–O stretch (1104 cm^{-1}) and the wagging mode of the inserted CH_2 group (1048 cm^{-1}). The accompanying band at 1352 cm^{-1}, which is usually associated with the formation of $Si–CH_2–Si$, confirms that the Kumada rearrangement is occurring in PMS because the peak at 1050 cm^{-1} (usually stronger) is normally obscured by the oxidation peak. However, if the object is to establish the threshold temperature for the rearrangement, then the weak peak at 1352 cm^{-1} is not a reliable indicator —the more intense CH_2 wagging mode should be used instead. For silicon single-crystal wafer substrates, this mode is observed after heating for 1 h at 150 °C, while the CH_2 wagging was only detected after heating the sample (as deposited thin film) for 1 h at 300 °C in inert atmosphere.

Significant variations were observed in the ratio of the integrated intensities of the antisymmetric and symmetric C–H stretching modes during pyrolysis of the deposited layer on silicon substrates. The degree of conjugation in the σ bonds of the polymer backbone is presumably affected by the nature of the inserted group. The polarizability of the silicon electronic shell facilitates transmission of the electronic demands of the inserted group toward the C–H bond. The participation of vacant nd orbitals in σ and d_π/p_π interactions has been proposed to explain the observed effects in M–X bonds of compounds such as MX_nR_{4-n} (M = Si, Ge, Sn, Pb; R = alkyl radical), where X is an atom with lone pairs. However, the current theoretical consensus is that d_π/p_π bonding is negligible in silicon compounds.[14,15] In our case, there is apparently a long-range effect through a Si–C bond from the conjugated chain. The effect is still detectable, not in terms of band positions, but in the ratio of the integrated intensities of the symmetric and antisymmetric C–H stretching modes. The integrated IR intensities (A) of the Ge–H stretching modes in the IR spectra of triorganogermanes (R_3GeH) are related to the sum of the Taft constants (σ) of the substituents and so the intensities of the bands in alkyl-substituted compounds can considered to be indicative of the σ–σ conjugation effect. Finally, the 967 cm^{-1} peak that appears during the oxidation can be associated with the 964-cm^{-1} peak in crystalline SiC, which has previously been attributed to the formation of a Si–O–C phase.[20]

Pyrolysis of PMS Deposited on Single-Crystal Silicon Wafers. The insertion of CH_2 groups into the Si–Si bonds in PMS clearly takes place at temperatures well below 400 °C. Moreover, even after pyrolysis for 1 h at 450 °C under inert atmosphere, the polymer does not totally lose its reactivity towards oxygen. The presence of oxygen could not be completely eliminated but the sharpness of the Si–O stretch at 1104 cm^{-1} still permitted observation of the CH_2 wagging mode at 1042 cm^{-1}. At 380 °C, a new peak appeared at 1311 cm^{-1}, accompanied by a shoulder on the antisymmetric C–H bend of the CH_3 group at 1409 cm^{-1} . These two new peaks were not detected for PMS pyrolyzed at 300 °C (even after 8 h) or upon prolonged exposure to air. The intensity of the antisymmetric deformation of the methyl group is decreased if insertion is not complete and the polymer is subject to oxidation. Finally, the C–H stretching bands become broad, probably due to overlapping of the new C–H stretching modes of the methylene group.

Conclusions

Polymethylsilane can be readily used as a direct pyrolytic precursor to the formation of SiC layers on silicon single-crystal wafers. The polymer undergoes the Kumada rearrangement at temperatures below 200 °C, and its chains preserve an unexpected high mobility on the substrate. Multiple internal reflection IR spectroscopy inside the thin layers of the material deposited on silicon single-crystal wafers can be conveniently used to monitor the transformation of PMS into PCS. Separation of the vibrational spectroscopic changes due to pyrolysis from those due to oxidation during the PMS → PCS transformation in the 100–450 °C range is a necessary step in any accurate interpretation of the process because of the high sensitivity of PMS toward oxidation. On the basis of absorption coefficients, the final stages of the Kumada rearrangement are best followed by monitoring the behavior of the CH_2 group scissors vibration, while the CH_2 wagging mode is a better probe for the initial stages of the rearrangement. Separation of the oxidation effects from those due to pyrolysis is possible when the starting polymer exhibits a low degree of oxidation.

Acknowledgment. We thank to Dr. Graham McKinnon of Alberta Microelectronic Center for providing the silicon single-crystal wafers used in this study. This research was supported by the following agencies: FCAR (Quêbec) and NSERC and EMR (Canada).

---

[20] Lee, S. Y.; Hench, L. L. In *Ultrastructure and Processing of Advanced Structural and Electronic Materials*, Noyes Publications: Park Ridge, NJ 1983; 171.