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Layered polysilane: thermolysis and photoluminescence

J. He, J. S. Tse,* D. D. Klug and K. F. Preston

Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Canada K1A 0R6

Layered polysilane (Si_6H_6) and its thermolysis have been studied using FTIR spectroscopy, thermogravimetry/differential thermal analysis, mass spectrometry, electron paramagnetic resonance, Si K-edge absorption and photoluminescence spectroscopy. It is found that cross-linking between $(–Si_6H_6–)_n$ layers occurs through dehydrocoupling reactions when the layered polysilane is heated under vacuum or an inert atmosphere at temperatures of 100–200 °C. Structural changes in the silicon network are evident during thermolysis: the layered structure of polysilane starts to collapse at 200 °C and is transformed to amorphous hydrogenated silicon and subsequently to crystalline silicon (c-Si) at temperatures higher than 450 °C. This process is accompanied by the evolution of H_2 and SiH_4 gases. The resulting layered polysilane exhibits strong room temperature photoluminescence at 560 nm (*ca.* 2.2 eV) and a blue-shift of Si K-edge absorption (0.6 eV) relative to c-Si. Annealing the layered polysilane results in red-shifts of luminescence peak energy with the increase of annealing temperature, consistent with the trend observed in the Si K-edge absorption measurement. These results are interpreted in terms of the growth of silicon network dimension during the thermolysis. The reduction in visible luminescence intensity for the annealed product at 300 °C (or higher) is further attributed to the creation of defects, *e.g.*, silicon dangling bonds ($g=2.0047$) which provide pathways for non-radiative recombination. The relationship between layered polysilane (as well as its annealed products) and porous Si is discussed.

Speculation on the origin of intense light emission from porous silicon (por-Si)[1] has stimulated renewed interest in the structure and physical properties of siloxene.[2–5] It was shown previously that the siloxene might be the microstructure responsible for this interesting phenomenon in por-Si. The general consensus is that the luminescence is due to the quantum-confined effect.[1,6] Siloxene has commonly been referred to a layered polymer with the empirical formula $Si_6H_{6-x}(OH)_x$. Prepared by the topochemical hydrolysis reaction of $CaSi_2$ with aqueous HCl, its oxygen content varies with preparation conditions.[5,7] The starting material $CaSi_2$ consists of alternating Ca layers and corrugated Si(111) planes in which Si_6 rings are interconnected to each other.[8] It is surmised that during reaction the Ca atoms are topochemically removed, leaving the Si_6 rings basically intact and satisfying the remaining Si dangling bonds by H or OH or O linkage groups. A number of structural investigations of this material have been reported.[9–11] Based on X-ray diffraction measurement, Weiss *et al.* proposed a structural model for siloxene consisting of stacked corrugated Si(111) layers with substituent H and OH groups.[10] A disordered structure with O-substitution within the Si layer and oxygen cross-linking between the layers has also been proposed.[11]

We have recently examined the structure of siloxene prepared under different conditions.[5] Our XRD results show that oxygen insertion into Si layers does not occur and that the Si(111) layers remain intact. Furthermore, siloxene prepared under controlled conditions (inert atmosphere and lower temperature) was found to have H-terminated Si(111) layers stacked to form a graphite-like crystal referred to as layered polysilane, Si_6H_6 (Fig. 1). Theoretical calculations indicate that Si_6H_6 has a direct band gap of about 3 eV. A weak indirect band gap approaching that of bulk silicon is developed in the cross-linked layered polysilane ($Si_{6n}H_6$) as the number of layers increases.[12] The similarity in band-gap structure between hydrogen-passivated por-Si and cross-linked layered polysilane ($Si_{6n}H_6$) has been noted.[12]

In the present work we explore the cross-linking of Si sheets of layered polysilane by thermolysis and study the luminescent properties of layered polysilane and its annealed products. The results establish a clear correlation between the luminescence behavior and the growth of the silicon network during thermolysis.

Experimental

The synthesis of layered polysilane followed the procedure described previously.[5] 4.0 g (0.0415 mol) of powdered $CaSi_2$ (*ca.* 5–20 mesh, Aldrich) were added to the mixture of aqueous HCl (37%) and absolute EtOH (1:1 v/v, total 100 ml) in a beaker at −20 °C. The mixture was continuously stirred for 4 h under an Ar atmosphere in a darkened room. In this process, black $CaSi_2$ powder was transformed to a green-

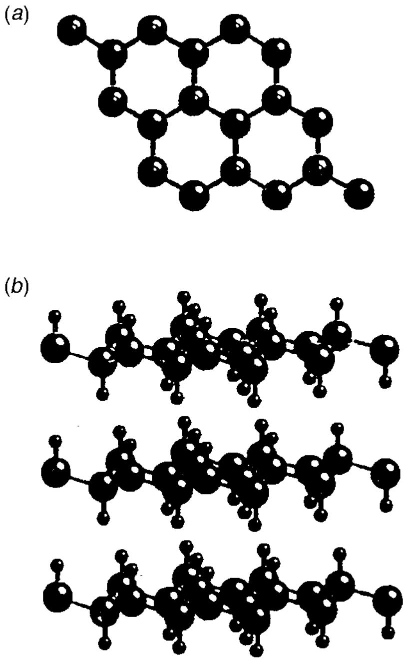


Fig. 1 Schematic representation of (*a*) a single polysilane layer viewed down the *c* axis; and (*b*) packing of layered Si_6H_6 polysilane in the crystal

yellow solid and hydrogen gas bubbling was also observed. After filtration and rinsing with EtOH, a greenish yellow solid product was obtained. Powder X-ray diffraction, Si near K-edge absorption and FTIR measurements indicated that some impurity of glassy SiO_x and/or SiO_xH_y phase was also present. Further purification was effected by rinsing with concentrated aqueous HF, followed by washing several times the sample with anhydrous methyl alcohol at *ca.* 0 °C under Ar. The yield of layered polysilane was *ca.* 30%. Elemental analysis showed that the resulting layered polysilane contained about 2 mass% F.

Annealed samples were prepared by heating the layered polysilane to a given temperature at *ca.* 2 °C min^{-1} and holding at that temperature for 1 h. They were then cooled slowly to ambient temperature and stored in a dry-box to await characterization.

Luminescence spectra were collected using an Ar^+ Coherent Innova 90 laser operated at a wavelength of 488 nm with the beam dispersed over 1 cm^2 sample area (10 mW cm^{-2}). Samples were placed as wafers inside a cell with fused silica windows that was evacuated to *ca.* 10^{-5} mbar. The emitted light was collected by a quartz lens and focussed on the entrance slit of a Spex 1403 monochromator. Appropriate cut-off filters were used to remove scattered excitation radiation. The output of the monochromator was monitored by a Hamamatsu model R928 multialkali cooled side-on photomultiplier tube operated at 1700 V. The luminescence data were acquired by use of a Spectracq multichannel analyzer which was interfaced to an IBM personal computer with Spectramax software.

Si K-edge absorption spectra were measured at the double-crystal monochromator (DCM) beamline of the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Center, University of Wisconsin-Madison. Details of the DCM monochromator have been described elsewhere.[13a] In essence, photons from the storage ring (1 GeV, *ca.* 100–150 mA) were monochromatized by reflection from two asymmetrically mounted InSb(111) crystals. Samples were mounted on indium foil (99.99% pure, Johnson Matthey) stacked on a stainless steel disk which was packed on an aluminium holder. They were then transferred to the ionization chamber. All manipulations were carried out under an inert atmosphere. Data were obtained using the total electron yield (TEY). At the photon energy of Si K-edge (*ca.* 1800 eV) the probing depth is *ca.* 700 Å.[13b] Therefore, the results obtained reflect the bulk characteristic of the sample. The energy resolution is *ca.* 0.9 eV. No charging was observed in the measurement.

IR spectra were recorded on a Bio-Rad FTS-40A spectrometer equipped with a N_2 purge assembly and a liquid-N_2-cooled mercury cadmium telluride detector. FTIR samples were prepared in a dry-box by finely grinding the solid samples with potassium bromide (KBr) in a boron carbide mortar and pestle, and pressing into pellets for absorption studies.

Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-12 spectrometer equipped with the usual devices for the readout of temperature, microwave frequency and magnetic field. Measurements were carried out at ambient temperature on *ca.* 0.2 g of sample in a 5 mm thin-walled Suprasil®. The unpaired spin count was estimated by comparing the integrated area under the EPR absorption curve with that from a weak pitch standard sample.

Thermogravimetry (TG) and differential thermal analysis (DTA) of layered polysilane was performed on a Seiko 220 TG–DTA instrument. A flow of N_2 (*ca.* 100 ml min^{-1}) was maintained during the TG runs. Samples (*ca.* 10 mg) were heated in an aluminium pan at a rate of 10 °C min^{-1} from 50 to 600 °C.

The evolution of volatile products during the pyrolysis of layered polysilane was monitored with a quadrupole mass spectrometer (UTI 100C Precision Mass Analyzer) using an ionization energy of 75 eV. Samples (*ca.* 10 mg) were placed in a quartz tube which was connected to the UHV chamber for mass detection. The quartz tube was heated at a rate of 10 °C min^{-1} from 100 to 500 °C. A scan from 1 to 150 u was collected every 1 min throughout the pyrolysis process. This apparatus permits the identification of the different gases evolved during thermolysis. The evolution of the ionic currents of the characteristic ions was plotted as a function of temperature. In the absence of standardization only qualitative information may be drawn from these curves.

Results and Discussion

IR study of layered polysilane

An earlier study showed that siloxene prepared by the reaction of $CaSi_2$ with aqueous HCl under stringent conditions (reaction temperature below 0 °C under Ar in a darkened room) has an X-ray diffraction pattern consistent with oxygen-free siloxene (Si_6H_6) together with an amorphous phase attributed to SiO_x-related species.[5] Fig. 2(*a*) shows the IR spectrum of this material, exhibiting absorption bands at 3405, 2098, 1621, 1040, 897, 796, 629, 525 and 512 cm^{-1}. The broad band centered at 3405 cm^{-1} is attributed to the (Si)O—H stretch, that appeared along with the O—H bending mode at 1621 cm^{-1}. This observation, indicative of the presence of $Si(OH)_x$ species, concurs with that reported previously.[10] The band at 2098 cm^{-1} is characteristic of the $(Si)_3Si$—H stretching mode.[3d,10,14,15] It appears that there is no oxygen insertion into the Si(111) planes, since no (O)Si—H band (*ca.* 2200 cm^{-1}) was found.[3d] The strong absorption band at 1040 cm^{-1} is due to the Si—O—Si stretch, suggesting the presence of SiO_x species. The sharp feature at 512 cm^{-1} has also been assigned to Si—O vibration.[16] The band at 897 cm^{-1} is attributed to SiH_2 shear mode.[3d] The presence of SiH_2 is not surprising, as the terminal Si atoms in the Si(111) planes need two H atoms to saturate. The band at 525 cm^{-1} has been attributed to Si—Si vibration in Si planes,[3d] this vibration is IR active as the Si(111) layers were puckered and unsymmetric. The origin of the band at 796 cm^{-1} is not clear currently, probably it may be associated with O—Si—O bending mode. These IR observations complement the results obtained from XRD measurements.

It is conceivable that layered polysilane is the primary product in the topochemical reaction and that its formation follows reaction (1):

$$3nCaSi_2 + 6n\ HCl \rightarrow [Si_6H_6]_n + 3n\ CaCl_2 \qquad (1)$$

The hydrolysis of Si—H bonds results in $Si(OH)_x$ and further

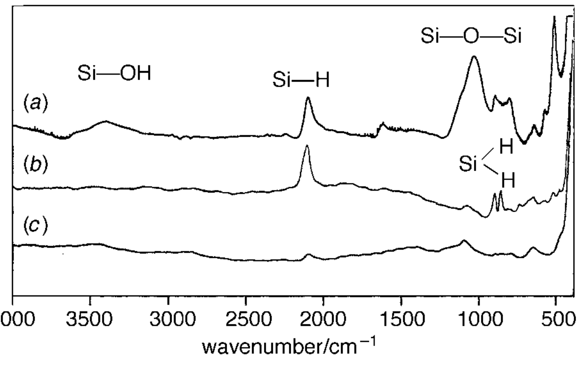


Fig. 2 FTIR spectra for (*a*) 'siloxene' isolated from the topochemical reaction of $CaSi_2$ with HCl under controlled conditions; (*b*) layered polysilane obtained by rinsing 'siloxene' with HF; and (*c*) annealed product by heating layered polysilane under a N_2 atmosphere at 300 °C

condensation of SiOH leads to the formation of SiO_x:

$$\equiv Si-H+H_2O\rightarrow \equiv Si-OH+H_2 \tag{2}$$

$$2\equiv Si-OH\rightarrow \equiv Si-O-Si\equiv +H_2O \tag{3}$$

Apparently, reactions (2) and (3) are accelerated by excessive heating and exposure to air. Therefore, they can be minimized under controlled conditions, such as at lower temperature (<0 °C) and under an inert atmosphere.

The impurity $Si(OH)_x$ and SiO_x can be removed by rinsing with concentrated aqueous HF followed by washing several times with anhydrous methyl alcohol. These species react with HF to form H_xSiF_{6-x} ($x \leqslant 2$), which is soluble in methanol and can be effectively removed from the residual insoluble powder. Fig. 2(*b*) shows the IR absorption features of the resulting material, layered polysilane. Very little, if any, OH and SiO associated species are present. The prominent IR absorptions for layered polysilane are 2100 cm^{-1} for $(Si)_3Si-H$ stretching mode, 899 cm^{-1} for SiH_2 shear and 859 cm^{-1}. The latter band is within the SiH_2 wagging mode[3d,15] and can therefore be assigned to a SiH_2 vibration. Other absorptions at 651 cm^{-1} for Si—H bending and 525 cm^{-1} for Si—Si in-plane vibration are still observable. It is known that the H-terminated Si(111) surface is virtually inert to attack by hydrofluoric acid at low pH.[17] This may explain the relative stability of layered polysilane toward concentrated HF solution during the purification process. Layered polysilane is relatively stable in solvents such as alcohols at temperatures below 0 °C. However, it ignites spontaneously on contact with air at ambient temperature. This is the typical behavior of molecular silanes and is reminiscent of the known 'lepidoidal silicon' prepared by the reaction of $CaSi_2$ with $SbCl_3$ in dichlorobenzene[18] or IBr in CCl_4.[19]

Thermolysis

A thermolysis study was undertaken by heating the samples of layered polysilane to a final temperature under a N_2 atmosphere. The resulting solid was pressed into a pellet and examined by FTIR. The intensity of the Si—H stretching mode around 2100 cm^{-1} decreases with increasing thermolysis temperature, as does that of the SiH_2 vibrations. IR data of the 300 °C sample [Fig. 2(*c*)] show the absence of bands for the SiH_2 species (899 and 859 cm^{-1}) and Si—Si in-plane vibration (525 cm^{-1}), but the absorptions of Si—H (2100 and 651 cm^{-1}) are still visible. This observation suggests that a dehydrogenation reaction occurs during heating in which the layered structure collapses and the Si—Si in-plane vibration is lost.

Further insight into the thermochemistry was obtained by separate thermogravimetry (TG) and mass spectroscopy (MS) measurements, as shown in Fig. 3. The TG curve shows mass loss for layered polysilane during the thermolysis from 50 to 600 °C, and MS qualitatively analyzes the gases evolved in this process. From ambient temperature to 200 °C, a small mass loss (2%) was observed. Hydrogen was detected as low as 100 °C with maximum evolution at 160 °C, indicating the occurrence of dehydrogenation reactions. From 200 to 300 °C, a mass loss of 12% corresponded to the evolution of SiH_4 and slight escape of H_3SiF and H_2, suggesting that both fragmentation and dehydrogenation reactions take place. No higher silane derivatives such as Si_2H_6 and Si_3H_8 were found by MS. SiH_4 was identified by the appearance of molecular fragments of m/z 30 (SiH_2^+, most abundant, shown in Fig. 3), m/z 31 (SiH_3^+) and m/z 32 (SiH_4). H_3SiF was characterized by the presence of molecular fragments at m/z 46 ($SiHF^+$), m/z 47 (SiH_2F^+, most abundant, shown in Fig. 3) and m/z 48 (SiH_3F). The incorporation of F was clearly minimal (*ca.* 2 mass% by elemental analysis) and arose from the HF rinsing. A further small mass loss (2%) observed from 300 to 450 °C resulted from the evolution of H_2 and residual SiH_4.

Hydrogen evolution below 200 °C most likely arose from a dehydrogenation reaction involving adjacent $[Si_6H_6]_n$ layers:

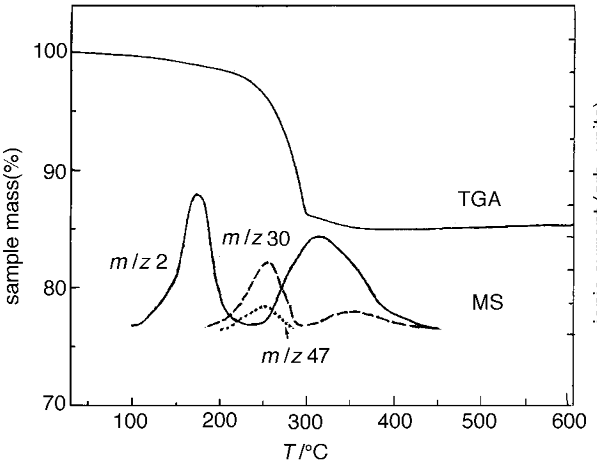
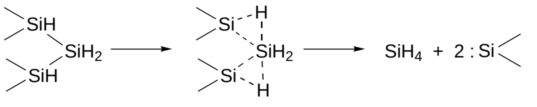


Fig. 3 Thermogravimetric analysis and mass spectrometry for layered polysilane. The ion signal at m/z 2 (—) arises from H_2; m/z 30 (---) from SiH_4; and m/z 47 (•) from H_3SiF.

$$\equiv Si-H+\equiv Si-H\rightarrow \equiv Si-Si\equiv +H_2 \tag{4}$$

The interlayer distance between Si—H•••H—Si is only about 2.0 Å.[20] This facilitates the interlayer dehydrocoupling reaction.

During thermolysis, the evolution of SiH_4 started at 180 °C and reached a maximum at 260 °C. The complete loss of the SiH_2 vibration band in the IR spectrum for the annealed product at 300 °C suggests that the SiH_2 group is involved in the fragmentation reaction. It has been reported that silane oligomers decompose *via* 1,2-hydrogen shift reactions to form silanes and silylenes in the temperature range 250–350 °C.[21,22] A similar mechanism may account for the evolution of SiH_4, involving a double 1,2-H shift with a five-coordinate transition state and the generation of silene species. The evolution of H_3SiF could proceed in a similar manner [eqn. (5)].



(5)

Differential thermal analysis (DTA) was conducted concurrently with the TG measurement. In Fig. 4 the DTA curve for the layered polysilane exhibits a large exotherm at *ca.* 290 °C. This fact indicates that a major structural change occurs near 290 °C. The transformation from a metastable layered structure to an amorphous form would be expected to be highly exothermic, and powder X-ray diffraction confirmed that the

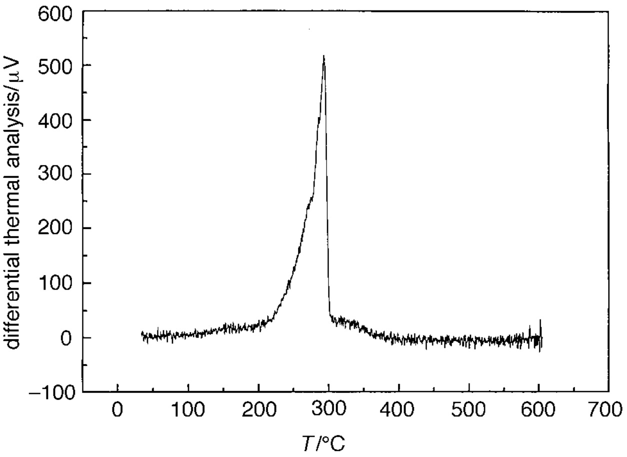


Fig. 4 Differential thermal analysis for layered polysilane, showing that a large exotherm occurred in the range 220–295 °C

product at 300 °C was amorphous. The IR data [Fig. 2(*c*)] provide further evidence for the structural change in the loss of the Si—Si in-plane vibration.

At temperatures higher than 300 °C, cleavage of the Si—H bond becomes possible, leading to the formation of H· and ≡Si· radicals. The H· radical will further abstract another proton from ≡Si—H groups to form H_2.

$$\equiv\text{Si—H} \rightarrow \equiv\text{Si}\bullet + \bullet\text{H} \qquad (6)$$

$$\text{H}\bullet + \text{H—Si}\equiv \rightarrow \equiv\text{Si}\bullet + \text{H}_2 \qquad (7)$$

The hydrogen evolution stops when the pyrolytic temperature reaches *ca.* 450 °C, at which point crystalline silicon is formed according to XRD measurement.

To ascertain the presence of ≡Si· radicals during the thermal process, we used EPR spectroscopy to measure the *g*-value and spin count of paramagnetic centers in the resulting solid. Fig. 5 shows the EPR spectra for the as-prepared layered polysilane and the pyrolytic product at 300 °C. The signal with $g = 2.0005$ is due to the impurity in the sample cavity. The as-prepared layered polysilane showed a resonance with $g = 2.0047$ and linewidth of *ca.* 5 G, which correspond very closely with the parameters for disilylsilyl and trisilylsilyl radicals.[23] As the structure of layered polysilane is well ordered, the paramagnetic center should be very localized or molecular-like. We are inclined, therefore, to assign the resonance to the silicon dangling bond $(\text{Si})_3\text{Si}\cdot$. The unpaired spin count for this defect was *ca.* 3×10^{14} spin g^{-1}, *i.e.* comparable to siloxene prepared from the reaction of $CaSi_2$ with aqueous HCl.[24] It is likely that some silicon dangling bonds were not saturated by H^+ during the disintercalation of Ca^{2+} from silicon layers (reaction 1). Heating the layered polysilane to 200 °C, the spin count of the resulting solid scarcely changed. However, the spin count increased to 2×10^{16} spin g^{-1} and the linewidth became broader (*ca.* 8 G) in the sample annealed at 300 °C. This observation supports the hypothesis of dehydrogenation reaction through cleavage of the Si—H bond at 300 °C [reactions (6) and (7)]. It is interesting to compare the *g*-value obtained here to that observed in hydrogenated amorphous Si (a-Si:H). It has been reported that the *g*-value for the Si dangling bond in a-Si:H ranged from 2.004 to 2.0055, depending on hydrogen content, defect density and other sample preparation conditions. As the hydrogen content is increased from 10 to >30 atom%, the band gap is increased from 1.7 to *ca.* 2.5 eV, and its *g*-value is decreased from 2.0055 to 2.004.[25] In our case, since the hydrogen content in annealed polysilane is high (>10 atom%, <50 atom%), the assignment of the $g = 2.0047$ (*ca.* 8 G linewidth) resonance to Si dangling bond is reasonable. This also further suggests that the annealed sample has a-Si:H-like structure.

Si K-edge absorption and photoluminescence

Our earlier study showed that the Si K near-edge X-ray absorption fine structure (NEXAFS) of layered polysilane bears a remarkable resemblance to that of porous silicon (por-Si).[5,26] In particular, the K absorption edges of these two materials are shifted to higher energy relative to (c-Si). Since the K absorption edge measures the energy separation between the 1s core level and the minimum of the conduction band (LUMO), a blue-shift in the absorption edge is indicative of the enlargement of band gap (HOMO−LUMO). In Fig. 6, the Si K-edge absorption spectra for layered polysilane and its annealed products at 200 and 300 °C are compared with c-Si. The absorption edge for layered polysilane is *ca.* 0.6 eV above that of c-Si and the shift is about 0.4 eV for the annealed product at 200 °C. Almost no shift (*ca.* 0.1 eV) is found for the annealed product at 300 °C. Evidently, the absorption edge for the annealed product is red-shifted with increase of annealing temperature. This trend can be readily explained in terms of the cross-linking of the silicon network with increase of annealing temperature. In layered polysilane, the silicon network is best described as a two-dimensional structure. By contrast, in the annealed product at 200 °C, it is better described as a partially cross-linked layered network similar to por-Si. With the collapse of the layered structure in the annealed product at 300 °C, it takes on the bulk-like amorphous form. The presence of hydrogen and a Si K absorption edge coincident with that of a-Si as well as no X-ray powder diffraction suggest that the structure of this annealed product resembles hydrogenated amorphous silicon.[26,27]

Photoluminescence (PL) measurements were carried out at room temperature. It was noted that the PL intensity of layered polysilane (before thermal annealing) lost about 50% after 20 min irradiation at 10 mW cm^{-2}. Other annealed samples also showed a certain degree of PL fatigue with prolonged irradiation. Such PL fatigue has also been observed in siloxene[11] and in a-Si:H.[28] The PL spectra shown in Fig. 7 were recorded before a substantial loss of PL intensity was reached. As is shown in Fig. 7, layered polysilane displays a strong visible photoluminescence with peak energy at 560 nm. Similar photoluminescence has also been observed in 'quasi'-two-dimensional σ-conjugated organosilicon polymers such as polysilynes[29] and ladder polysilanes.[30] The emission mechanism in organopolysilanes has been described as Si—Si σ^*–σ

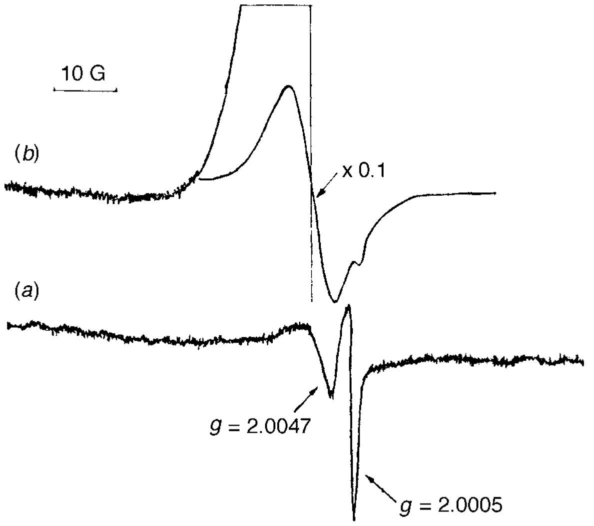


Fig. 5 EPR spectra for (*a*) layered polysilane, (*b*) annealed product at 300 °C

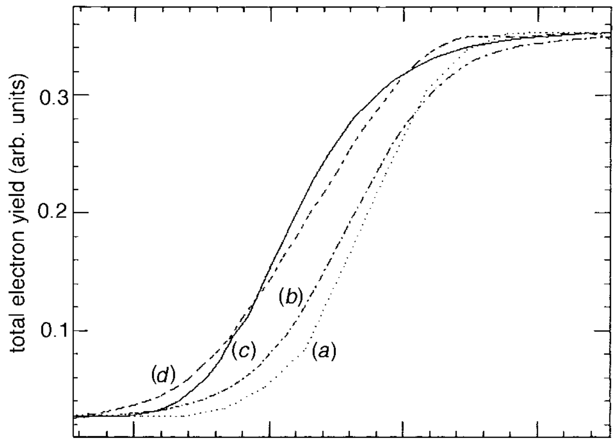


Fig. 6 Si K-edge absorption for (*a*) layered polysilane (•); (*b*) annealed product at 200 °C (–·–); (*c*) annealed product at 300 °C (—); and (*d*) c-Si (---)

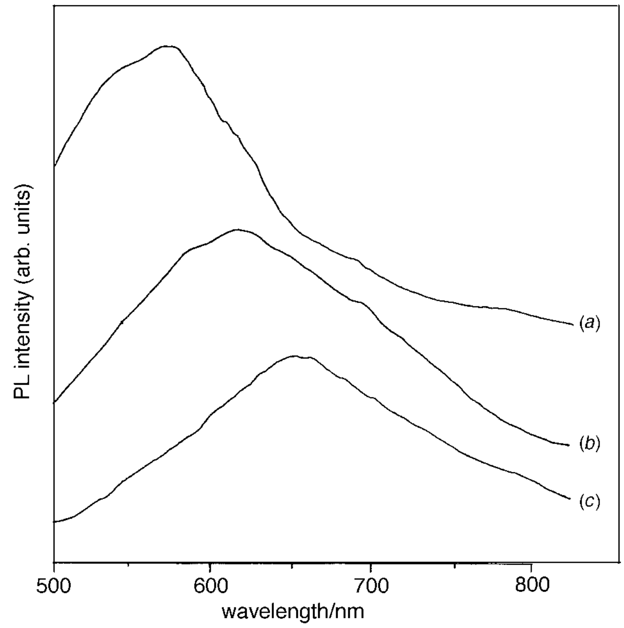


Fig. 7 Photoluminescence spectra for (*a*) layered polysilane; (*b*) annealed product at 200 °C; and (*c*) annealed product at 300 °C

deexcitations.[31] This electron–hole pair recombination process is often used to interpret the bandtail emission observed in amorphous semiconductors.[29,32] A similar electron–hole recombination model may be employed to account for the visible luminescence in layered polysilane. As theoretical calculations have shown that layered polysilane possesses a direct band gap,[12] this electron–hole pair recombination is expected to be strongly radiative.

With increasing annealing temperature, the luminescence band broadens progressively and the peak shifts to lower energy. This trend is again related to the cross-linking of the Si network. By annealing at 200 °C, the layers are partially cross-linked through a dehydrocoupling reaction. In such a Si structure, an indirect band gap is developed and direct radiative transition is weakened, as shown by the theoretical calculations.[12] However, the Si K-edge absorption still shows some band gap enlargement, as the absorption edge is blue-shifted with respect to c-Si. As in por-Si, quantum confinement effects widen the band gap and thus bring the optical transitions into the visible range; at the same time it enhances the visible luminescence efficiency by reducing the probability of non-radiative electron–hole pair recombination in the confined zone.[33]

Only very weak photoluminescence is found for the annealed sample at 300 °C. On the one hand, the Si K absorption edge does not show a significant blue-shift relative to c-Si, so that the visible photoluminescence is expected to be very weak at room temperature. On the other hand, the silicon structure of this material resembles a-Si:H. It is known that a-Si:H exhibits photoluminescence in the visible region. The peak energy of the PL in a-Si:H ranges from 1.3 to 2.05 eV with increasing hydrogen content (2–40 atom%).[34] However, the high density of silicon dangling bonds found in this material may serve as non-radiative pathways for electron–hole recombination, hence, the luminescence intensity is significantly reduced.

It is known that the surface of por-Si freshly prepared by anodic electrochemical etching of c-Si in HF solutions is passivated with hydrogen, with minimal amount of oxygen presence.[6,33a] Por-Si luminesces in the ranges between 550 and 900 nm. By thermal annealing in vacuum or under inert atmosphere, the photoluminescence peak energy shows progressive red-shifts with increasing temperature of annealing, and its intensity decreases simultaneously.[35] Furthermore, the Si K absorption edges for both layered polysilane (or multiply linked polysilane) and por-Si are blue-shifted by *ca.* 0.4–0.6 eV with respect to c-Si. These strong resemblances in compositions and properties observed in both por-Si and layered polysilane suggest that the nanostructure of por-Si may be predominently composed of layered Si sheets, as in polysilane or in the multiply linked polysilane. Indeed, it has been suggested that the luminescing chromophore is originated from nanocrystalline Si, such as (100)-faceted cube.[36] Our study clearly shows that layered polysilane (or multiply linked polysilane) may serve as a structural model for por-Si, in good agreement with a recent X-ray fluorescence study of por-Si.[37]

Summary

We interpret our observation on Si K-edge absorption and photoluminescence properties in terms of a structural evolution of the silicon network during thermolysis of layered polysilane. Annealing layered polysilane at temperatures below 200 °C leads to the cross-linking between layers with the elimination of hydrogen. This cross-linked silicon network exhibits a blue-shift of the Si K absorption edge (0.4 eV) relative to c-Si and strong room-temperature visible photoluminescence, thereby resembling porous silicon. Consistent with the cross-linking of the silicon network, the Si K absorption edge and luminescence peak energy red-shift with increasing temperature of annealing.

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