Structure of siloxene and layered polysilane (Si_6H_6)

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Powder-x-ray-diffraction measurements on siloxene and calculations of the diffraction patterns for the three commonly proposed structures of siloxene ($Si_6H_6O_3$) clearly show that only a structure with silicon layers is ever observed. The formation of siloxene from $CaSi_2$ is topotactic, with the Si layers remaining intact and with no oxygen insertion into these layers. Siloxene prepared at 0 °C has very little oxygen incorporated into the interlayer gaps, and can be described as hydrogen terminated silicon layers (Si_6H_6), which we call layered polysilane. Layered polysilane can be purified by reaction with aqueous HF and is pyrophoric on contact with air. In some sense, layered polysilane can be considered the silicon equivalent of graphite.

INTRODUCTION

The efficient visible luminescence observed in porous Si has been attributed by different researchers to two effects. One explanation is the presence of nanometer-scale Si structures in porous Si, in which quantum-size effects occur.[1-3] The other explanation involves the presence of chemical species such as siloxene on the surface of the porous Si particles.[4-6] The luminescence is then attributed to the siloxene. In order to understand the luminescence of siloxene, it is a prerequisite to understand the atomic structure of this compound. However, there are three commonly proposed structures for siloxene, with little structural evidence for two of them.

Recently Deak et al.[7] showed how the visible luminescence of siloxene could be explained by "chemical quantum confinement" of Si by oxygen in two of the three proposed structures of siloxene (see Fig. 1). In these two structures, shown in 1(b) and 1(c), oxygen atoms are incorporated within the silicon sheets. However, these two structures have never been confirmed by a diffraction experiment. Here, we present, to our knowledge, the first diffraction data and calculated diffraction profiles for siloxene samples prepared in several ways. Only one basic structure type is ever observed [that shown in Fig. 1(a)] with silicon layers exactly as in $CaSi_2$. This structure is in agreement with the structure proposed by Weiss, Beil, and Meyer,[8] based on diffraction measurements. Therefore, an alternative explanation for the luminescence of siloxene is needed because Deak et al.[7] base their arguments on structures which are most likely fictitious.

Van de Walle and Northrup[9] recently calculated the band structure of siloxene in structure A [Fig. 1(a)] and of hypothetical Si_6H_6 layers assuming an interplanar separation of 4.75 Å. In their Si_6H_6 structure, a Si(111) layer is terminated above and below by H atoms. This is identical to structure A with the oxygen atoms removed. Van de Walle and Northrup calculated a band gap of 2.75 eV for Si_6H_6 and 1.7 eV for $Si_6H_6O_3$. In our experiments described below, we present the first evidence for Si_6H_6 layers (layered polysilane) in siloxene samples prepared at 0 °C.

EXPERIMENT

Siloxene samples were made by reacting powdered $CaSi_2$ (Aldrich) with aqueous HCl. For some samples the reactions were carried out at 80 °C for 30 min, while for others the reactions were carried out at 0 °C for the same time. The powders were then rinsed with water and freeze dried in a sample chamber which could be directly transferred to an argon-filled glove box. Some of the samples prepared at 0 °C were rinsed with aqueous HF to remove silicon oxides. All synthesis operations were carried out in a darkened room. All samples were stored in the glove box in opaque vials. A typical synthesis produced 5 g of product. The samples prepared in the ice synthesis were found to spontaneously combust upon exposure to air. Special procedures were adopted for measurements on this material.

X-ray-powder-diffraction measurements were made using a Siemens D-5000 diffractometer equipped with a copper target x-ray tube. For the samples made at 0 °C, a holder with a vacuum-tight beryllium x-ray window (25 μm thick) was filled and sealed within the glove box. The other samples were stable enough in air to be measured normally, although they too did oxidize but on a time scale of days as we show later.

IR absorbance measurements in transmission geometry were made on the air-stable samples using a Nicolet Fourier transform infrared (FTIR) spectrometer by pressing small amounts of siloxene and dry KBr into pellets. Photoluminescence measurements were made with a Photon Technologies (South Brunswick, NJ) LS-100 spectrometer on the air-stable samples.

Si K-edge x-ray absorption spectra were measured at the double crystal monochromator (DCM) beam line of
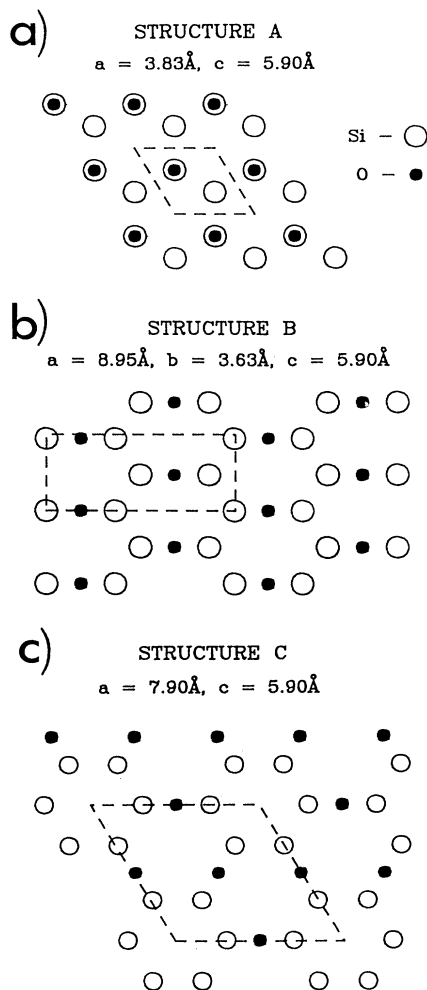
FIG. 1. Proposed structures for siloxene after Ref. 7. The oxygen atoms are the small solid circles and the silicon atoms are the open circles. Hydrogen atoms are not shown. The atom positions for a single siloxene sheet have been shown projected into the (001) plane. Appropriate unit cells for each structure are shown.
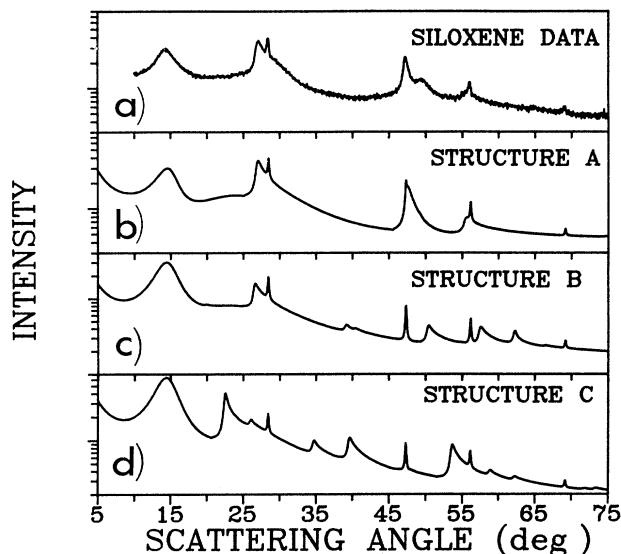

FIG. 2. Comparing the measured diffraction data of siloxene to calculations assuming random shifts or translations parallel to the layers between all adjacent layer pairs. (a) Data, (b) calculation based on structure A [Fig. 1(a)], (c) calculation based on structure B [Fig. 1(b)], and (d) calculation based on structure C [Fig. 1(c)]. The intensity scale is logarithmic.

the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Center, University of Wisconsin-Madison. Details of the DCM monochromator have been described elsewhere.[10] The energy resolution at the Si K edge is about 0.9 eV. Total electron yield[11] was employed to record the spectrum.

RESULTS AND DISCUSSION

Figure 2(a) shows measured x-ray diffraction data for the siloxene sample made at 80 °C. This material had ir absorbance in agreement with literature data for "as-prepared siloxene" (e.g., as in Fig. 11 of Ref. 5). The photoluminescence peaked near 550 nm, in agreement with the literature for "as-grown" siloxene (e.g., as in Fig. 1 of Ref. 12). Figure 2 also shows calculated patterns for siloxene taking structures A [Fig. 2(b)], B, [2(c)], and C [2(d)]. The scattering from hydrogen atoms is neglected,

neutral atom scattering factors for oxygen and Si (Ref. 13) are used and the standard geometrical and polarization factors[14,15] are included in the calculation.

The calculations were made assuming that Si-Si bond lengths were the same as in crystalline Si, Si-O bond lengths are 1.6 Å, and Si-O-Si contacts in structures B and C are linear. Bond angles for Si were chosen to be as close as possible to tetrahedral, but consistent with the hypothesized structures. The unit cells used for each structure are given in Fig. 1. The layer spacing, consistent with the data, was chosen to be 5.90 Å. Clearly, structure A is in best agreement with the data because the calculations for the other structures predict unobserved peaks. Small sharp Bragg peaks from crystalline Si near 28°, 47°, 56°, and 69° (an impurity in our $CaSi_2$) are included in the calculation to match the data.

The calculations also assume that there is a random rotation or translation parallel to the layers between every pair of adjacent layers, a characteristic known as turbostratic disorder. Such an assumption makes the calculations more complex but the methods are well known.[14,15] This assumption is needed to model the shape of the (100) peak near 27°, which is a characteristic "two-dimensional" peak.[16] The number of layers stacked and a fluctuation of the layer spacing to mimic strain are included as parameters in the calculation to fit the width of the (001) peak near 14.2°. The major region of disagreement between the data and the calculation in Fig. 2(b) (for structure A) is near the (110) peak at 47°. Figure 3 shows that this discrepancy can be eliminated if about 60% of adjacent layer pairs are stacked in registry with the center of a Si honeycomb directly above an Si atom in the next layer, and the remaining 40% of layer pairs
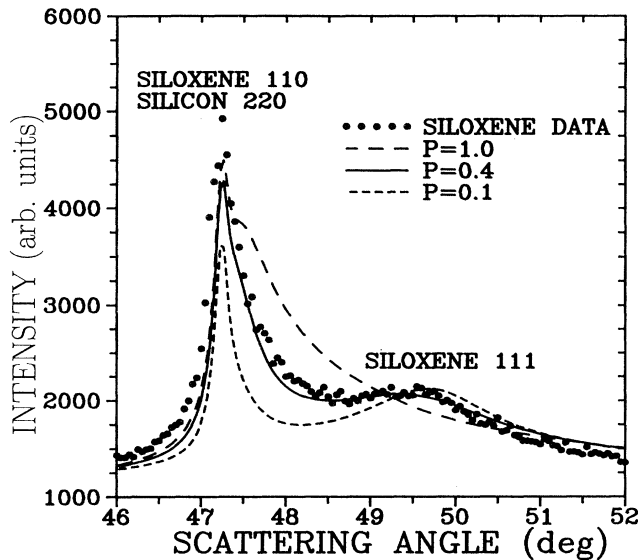
FIG. 3. Showing how the incorporation of registered stacking improves the agreement between data and calculation in the area of the (110) peak. P is the fraction of layers stacked with random shifts between adjacent layer pairs.

stacked randomly. This registered stacking has been suggested in the earlier work of Weiss, Beil, and Meyer.[8]

Figure 4 shows the complete calculation and fit to the data for siloxene prepared at 80 °C, based on structure A. Apart from the crystalline silicon, which is an impurity in our $CaSi_2$, the calculations match the data very well provided that the scattering from a glassy phase and a constant background are included. The contributions to the calculated curve from the glassy phase and from the crystalline silicon are shown also in Fig. 4. The glassy phase is probably amorphous SiO_x with x about 2 as we

will see from the x-ray absorption measurements below. A similar glassy phase with x about 1 can be prepared in pure form by heat treating siloxene to 400 °C in inert gas. This material is presumably similar to that suggested by Ubara et al.[17] Treatments at intermediate temperatures show mixtures of the glassy phase and siloxene (structure A), with the siloxene pattern disappearing above 300 °C in agreement with Ref. 17. At no temperature were patterns consistent with structures B or C ever observed.

All infrared measurements on fresh siloxene in the literature show Si-O-Si vibrational modes in apparent contradiction to structure A. However, all of our siloxene samples prepared according to the literature have significant amounts of the glassy phase as measured by x-ray diffraction. This helps to rationalize the IR results in the literature and for our samples since the glassy phase will have Si-O-Si contacts.

Figure 5 shows measured and calculated diffraction data for siloxene prepared at 0 °C (a), at 80 °C (b), and for a sample of the latter left exposed to light and air for 3 days (c). The patterns are visually quite different. The calculation for the exposed siloxene is identical to that of the 80 °C material from which it was made except that the relative intensity of the glassy phase peaks have been increased. This is evidence for the slow oxidation of the material directly to the glassy a-SiO_2 phase when exposed to light and air. The calculation for the material made in ice was made by removing the oxygen atoms from the structure and reducing the amount of glassy phase relative to Fig. 5(b). The oxygen atoms interfere destructively with the Si atoms at the (001) peak, so removing them is the best way to increase this peak intensity to match experiment. The good agreement with the data strongly suggests the existence of Si_6H_6 layers, which we call lay-
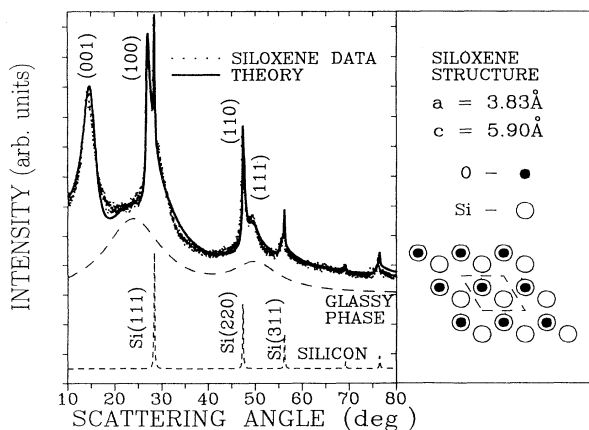

FIG. 4. (a) Calculated pattern for siloxene compared to the data. The calculation includes siloxene according to structure A, crystalline Si (an impurity in $CaSi_2$), and the glassy SiO_x phase referred to in the text. The contributions from each phase are shown in (b).
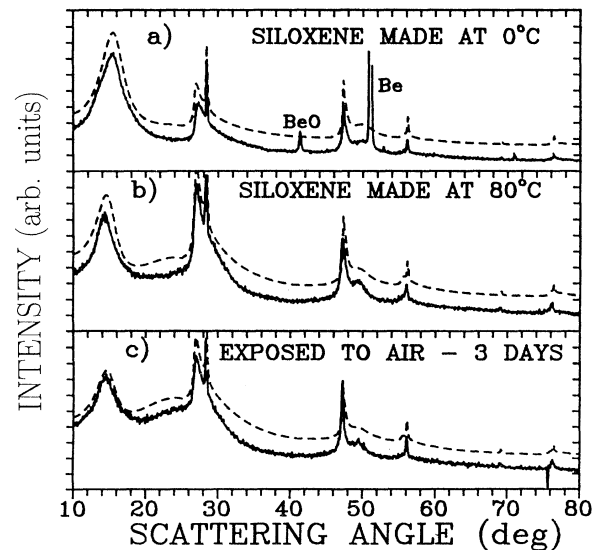

FIG. 5. Diffraction patterns and calculations for (a) siloxene prepared at 0 °C, (b) siloxene prepared at 80 °C [same as Fig. 4(a)], and (c) siloxene prepared at 80 °C, then left exposed to air and light for 3 days. The calculations have been offset vertically for clarity.

ered polysilane.

The layer spacing of layered polysilane differs from that of siloxene. To fit the data in Fig. 5(a), $c=5.50$ Å was used, while to fit the data in Fig. 5(b), $c=5.90$ Å was used. This change is caused by a shift of the (001) peak to larger angle in Fig. 5(a) compared to Fig. 5(b). The presence of the oxygen in the interlayer van der Waals gaps causes this expansion. The good fit in Fig. 4 does not necessarily *prove* that the siloxene structure contains OH groups in the interlayer gaps, only that oxygen, perhaps in Si-O bridges or as intercalated water, resides in the gaps. Moreover, the in-plane lattice constant is the same for both materials because of the strong Si-Si bond which is near 2.35 Å for most materials.

To further test for the existence of layered polysilane, we measured the Si K-edge absorption of siloxene prepared at 80 °C, and of siloxene prepared at 0 °C followed by HF rinsing and vacuum drying. The latter sample was transferred to the ultrahigh-vacuum (UHV) chamber using an argon-filled glove bag, as it is pyrophoric in air. All samples were measured at the same resolution. Figure 6 shows the spectra for crystalline Si (rinsed in HF before introduction into UHV), and the two siloxene samples. Notice that the absorption edge of the siloxene samples is shifted to higher energies relative to crystalline Si similar to that observed for porous Si samples.[2]

More important here is the larger peak near 1847 eV in the siloxene sample made at 80 °C, which is absent in the HF treated sample. The absorption spectrum of SiO₂ is dominated by exactly such a peak[18] suggesting that the siloxene prepared at 80 °C contains substantial SiO₂. This is consistent with the diffraction results for the sample made at 80 °C which requires a glassy component (prob-
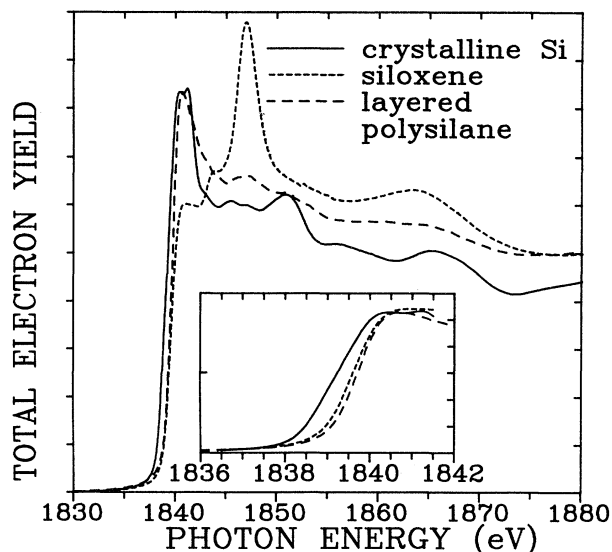
ably amorphous SiO$_x$) in the calculation to explain the measurement as shown in Fig. 4. The HF treated sample clearly contains little SiO₂ in agreement with other recent work.[18]

Infrared measurements made (to be published elsewhere) on the HF treated sample shows only Si-Si and Si-H vibrational modes with *no evidence* for Si-O-Si, Si-OH, or O-H modes. The sample was immersed in mineral oil (Nujol) for the measurement to avoid air exposure since the material is pyrophorric in air. This is taken as further evidence that the material is layered polysilane.

Figure 7 shows the x-ray diffraction pattern of the HF-rinsed material and two calculations assuming that the material is layered polysilane. The layer spacing was chosen to be 5.40 Å and the in-plane hexagonal lattice constant was 3.83 Å. No glassy phase is included in the calculation at all. Si atoms are located at $\pm(1/3,2/3,0.075)$ and H atoms are located at $\pm(1/3,2/3,0.28)$. This gives a Si-Si bond length of exactly 2.35 Å and a Si-H bond length of 1.15 Å. [This describes a Si(111) layer terminated above and below by H atoms.] The H atoms were included in the intensity calculation, even though their scattering power is very weak compared to Si. For one calculation the layers were stacked with a random shift (parallel to the layers) between each pair of layers. To fit the width of the (001) peak, a crystallite with ten Si-H sandwiches was used. Clearly the calculation assuming random stacking does not reproduce the peak shapes of the (100), (110), or (111) peaks, but the relative intensities of the peaks are well matched using the most reasonable structure for layered polysilane.

Also shown in Fig. 7 is the result of an improved calculation incorporating registered stacking shifts between

FIG. 6. K-edge x-ray absorption spectra for crystalline Si (solid line), siloxene prepared at 80 °C (small-dashed line), and for layered polysilane (long-dashed line). The inset shows the shift of the K edge for the siloxene and polysilane samples relative to crystalline Si.
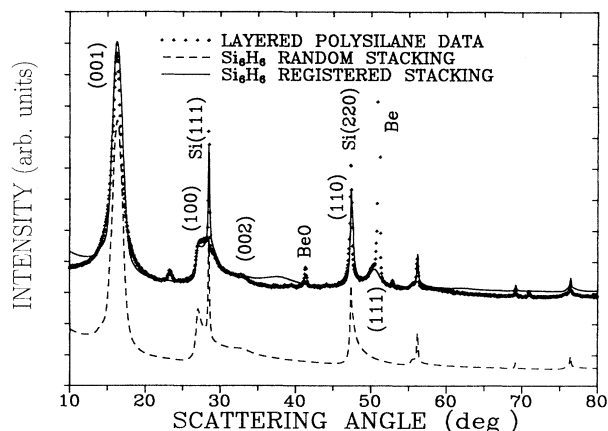

FIG. 7. The measured powder-x-ray-diffraction pattern for layered polysilane (dotted line) and two calculated patterns as described in the text. Random stacking of the Si₆H₆ layers is assumed in the lower calculation (dashed line) which has been shifted downward for clarity. Miller indices of the peaks from layered polysilane and crystalline Si (an impurity in our CaSi₂ are shown). Peaks from the beryllium window are indicated. The peak at 23.5 also arises from the Be window.

adjacent layers. For this calculation we assumed that random shifts were between 35% of adjacent layer pairs, and included registered shifts of $(+1/3,+2/3,0)$ (45%), $(-1/3,-2/3,0)$ (15%), and (0,0,0) (5%) between the remaining adjacent layer pairs. The rest of the parameters were kept the same as those in the other calculation shown. We do not claim to have determined the stacking sequence exactly, as other stackings give similar agreement. We stress, however, that the intensity ratios of the calculated peaks is in good agreement with the measured peaks. If other atoms (such as oxygen) are included in the interlayer gaps, the (001) peak is rapidly suppressed and such calculations cannot match the data.

The (001) peak of the layered polysilane (Fig. 7) is sharper than the (001) peak of the sample at 0 °C which was not HF treated [Fig. 5(a)]. The latter sample also had some glassy SiO_2 impurity present. Possibly, the glassy phase forms between the H-Si-H layers as the layered polysilane is oxidized, leading to interlayer strain [broader (001)] peak and an increased layer spacing.

The formation of silanelike layers during the reaction of $CaSi_2$ and HCl is consistent with the pyrophoric nature of molecular silanes which are flammable in air but stable in dilute mineral acids.[19] If no oxidation occurs, then the most natural reaction is an ion exchange

$$3CaSi_2 + 6H^+ \rightarrow Si_6H_6 + 3Ca^{2+} ,$$
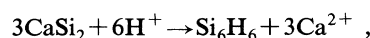
leaving the Si layers intact. Our data for the samples prepared at 0 °C are entirely consistent with this reaction. The layer spacing of the material prepared at 0 °C without HF rinsing is only 5.50 Å, the smallest ever reported for siloxene, again consistent with only a small amount of interlayer oxygen. The layer spacing for the layered polysilane (Fig. 7) is 5.40 Å.

Other workers have also proposed the existence of two-dimensional silicon-network compounds.[20] In Ref. 20 calculations of the band gap, E_g, of a variety of linear and planar silicon polymers gave $E_g = 4.0$ eV for linear polysilane $(SiH_2)_n$, $E_g = 2.5$ eV for a material apparently similar to the layered polysilane discussed here, and $E_g = 1.1$ eV for crystalline silicon. These results show the importance of the dimensionality of the silicon network on the resulting band gap. These ideas may be important in understanding the luminescence in porous Si.

CONCLUSION

To summarize, we have found that siloxene "as prepared" is only found in the layered-silicon structure shown in Fig. 1(a). There is no diffraction evidence for oxygen incorporation within the silicon layers as hypothesized in some earlier works [e.g., as in Figs. 1(b) and 1(c)]. Upon heating in inert gas or upon exposure to light and air it transforms to a glassy SiO_x phase with no diffraction evidence for the formation of the other two previously proposed siloxene structures at any temperature. Therefore, we believe that several of the siloxene structures proposed in the literature [i.e., those shown in Figs. 1(b) and 1(c)] have no experimental justification.

By preparing siloxene at 0 °C, we have been able to dramatically reduce the oxygen content of the material, and have prepared silicon layers terminated above and below by hydrogen atoms. This preparation step eliminates the glassy SiO_x impurity phase and also the oxygen in the van der Waals gaps. We call this exciting new material layered polysilane. Layered polysilane has hexagonal layers with an in-plane lattice constant of 3.83 Å. The layers are stacked with a layer spacing of 5.4 Å, and some random rotations or translations (turbostratic disorder) are found between adjacent layers. The fractional atomic coordinates of the Si and H atoms in the unit cell are Si at $\pm(1/3, 2/3, 0.075)$ and H at $\pm(1/3, 2/3, 0.28)$. Because of the similarity of this honeycomb-layered structure with that of graphite, layered polysilane can be considered the silicon equivalent of graphite.

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