Structure and optical properties of the planar silicon compounds polysilane and Wöhler siloxene

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The two-dimensional silicon backbone structure of planar polysilane and Wöhler siloxene is responsible for their exciting luminescing properties. We have prepared single crystals of siloxene by a topotactic reaction from crystalline $CaSi_2$. The chemical composition was determined as $[Si_6H_3(OH)_3]_n$. The x-ray crystal structure analysis identifies the so-called Wöhler siloxene as 2D-poly[1,3,5-trihydroxycyclohexasilane]. Polysilane exhibits the same structural properties but with a chemical composition $[Si_6H_6]_n$. The optical properties (infrared transmission, photoluminescence, excitation spectroscopy) of these well-defined materials are presented. A heat treatment above 350 °C in vacuum of Wöhler siloxene results in a destruction of the planar $\frac{2}{\infty}[Si^-]$ structure by internal rearrangements, which is evidenced by the x-ray-diffraction pattern and characteristic changes in the optical spectra. The involvement of Wöhler siloxene in the optical properties of porous Si is critically reviewed. [S0163-1829(97)02844-0]

I. INTRODUCTION

The discovery of the strong visible luminescence in porous silicon[1] has initiated a renewed interest in the optical properties of various silicon compounds and their possible use in optoelectronic applications. In particular, silicon-oxygen-hydrogen compounds, the siloxenes, exhibit a strong visible room-temperature luminescence, very similar to the luminescence from porous Si.[2] A recent review is given in Ref. 3. Unfortunately, the controversial discussion on the origin of the strong luminescence in porous silicon and the participation of siloxene was based on not properly defined siloxene samples. The knowledge about the chemical composition and the ground-state geometry is, however, a prerequisite to understand the optical properties of siloxene.

Siloxene is synthesized by a topotactical reaction from $CaSi_2$, a layered material with Si corrugated (111) layers that are linked by the Ca ions. During the synthesis the layered Si structure remains. Whereas most of the structural information on the siloxenes was developed intuitively by chemists,[4] there exist a few theoretical and experimental studies on three possible structures shown in Fig. 1. The structure depicted in Fig. 1(a) consists of Si(111) layers terminated above and below by OH groups and H atoms, respectively. In the other structures oxygen atoms are inserted in the Si plane leading to silicon wires [Fig. 1(b)] or to Si_6 rings separated by oxygen [Fig. 1(c)].

Deák et al.[5] presented calculations on the stability and energy-band structure of the different structures. The energetically most favorable configuration, which also was associated with the visible red photoluminescence (PL) in porous Si, was calculated to be the structure shown in Fig. 1(c). Similar results on the geometric and electronic band structure for the structure given in Fig. 1(a) are calculated by more sophisticated methods.[6] The planar structures Figs. 1(b) and 1(c) with oxygen in the planes were not studied in these calculations, because the energetically most favorable bond angle of Si-O-Si bonds deviates from 180°, which should lead to nonplanar configurations and a three-dimensional (3D) cross linking. However, in all structures the band structure is not very sensitive to the stacking of the layers but is largely determined by the structure within a single layer. Small siloxenic clusters exhibit already all necessary properties to explain the optical spectra.[7] In particular, clusters with oxygen bridging bonds exhibit the highest stability.

The geometrical structure of the so-called Wöhler siloxene (siloxene prepared according to the recipe given by Wöhler[8]) was first investigated by Weiss, Beil, and Meyer.[9] Although Weiss et al. claim that the structure of siloxene that they determined was prepared according to Kautsky[10] (Kautsky siloxene) their preparation is indeed identical to the Wöhler method. From their x-ray-diffraction data they propose the planar structure given in Fig. 1(a). The structural changes in Wöhler siloxene with thermal treatment were studied by Ubara et al.[11] A thermal anneal at 300 °C in vacuum destroys the two-dimensional ordered structure and transfers it into a three-dimensional disordered structure.

An elaborate x-ray-diffraction study was recently presented by Dahn and co-workers[12,13] on differently prepared Wöhler siloxene samples. The authors observe however only sharp x-ray-diffraction patterns from the 2D planar structure shown in Fig. 1(a). From their investigation Dahn et al. have severe doubts that the planar structures presented in Figs. 1(b) and 1(c) exist.

Several x-ray-absorption studies on siloxene are reported[12–16] and the oxidation state Si(+1) for Wöhler siloxene was established. But due to different sample treatments these papers also report controversial results.

In this paper, we present a study on the structural and optical properties of two-dimensional silicon layers, which are the backbone in Wöhler siloxene and planar polysilane. We will first describe a method to prepare crystalline siloxene with the ideal chemical composition $Si_6H_3(OH)_3$ and we shall identify the structure by powder and single crystal x-ray diffraction. The characteristic photoluminescence, infrared transmission and excitation spectra of this material will be presented and compared to those of layered polysilane. The structural and optical changes of these materials after annealing in vacuum are presented and the involvement of the annealed compounds in the strong visible luminescence from porous silicon is discussed.
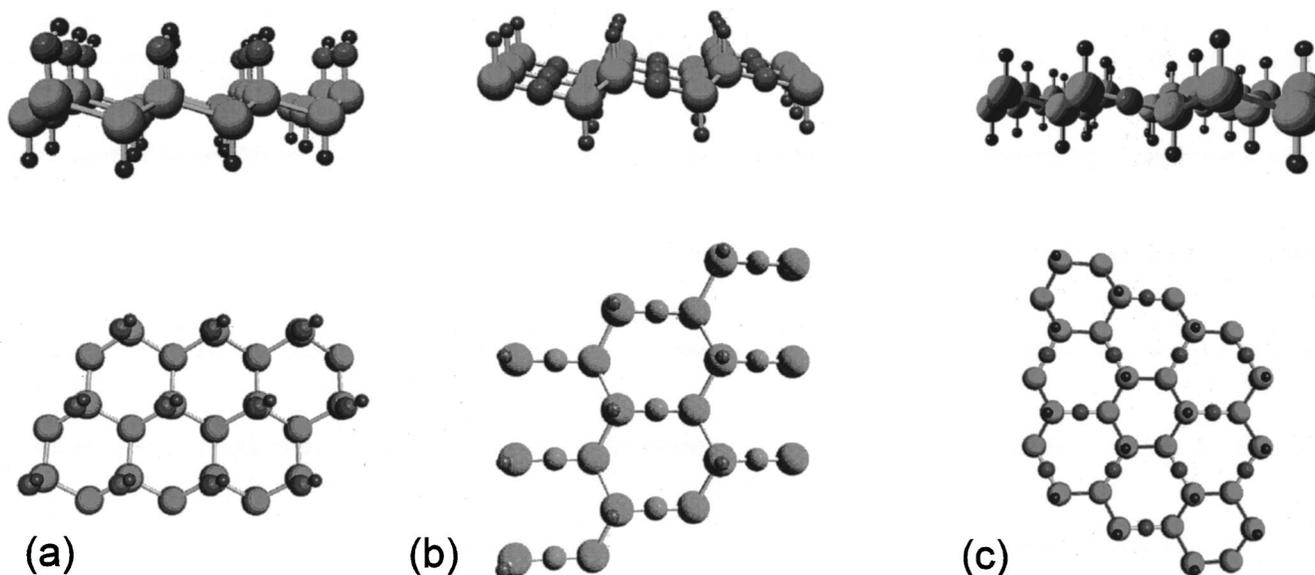
FIG. 1. Structural models of the different modifications of siloxene ($Si_6O_3H_6$): (a) Si planes terminated by H and OH groups, (b) Si chains and (c) Si_6 rings interconnected via oxygen bridges and terminated by hydrogen. Light colored atoms symbolize Si, small dark atoms hydrogen and larger dark atoms oxygen.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

A. Sample preparation

The siloxene samples were prepared according to the method described by Wöhler.[8] The starting material for the siloxene is the Zintl phase $CaSi_2$ in solid form. $CaSi_2$ exists in three crystallographic modifications, namely TR3 and TR6, which are both trigonal rhombohedral and differ by their stacking sequences, and one metastable, high-pressure tetragonal modification.[17–19] The commercially available $CaSi_2$ consists of the two modifications TR3≈65% and TR6 ≈35%. We also used the pure modification TR6 for the synthesis of siloxene, without any differences in the optical data of the final product.

We have optimized Wöhlers method of preparation with respect to the reproducibility of the chemical analytical results. About 100 mg of selected $CaSi_2$ crystallites (Aldrich) with faces of ≈10 mm^2 were immersed in 2 ml 37% HCl (p.a.) and stored under argon ambient in a dark tube at 0 °C. After a reaction time of 3 h the resulting bright yellow layered compound was filtered off and washed with deionized water (O_2 free, saturated with Ar inert gas) at 0 °C to remove Ca and Cl ions (Cl test with $AgNO_3$). The free Cl was removed totally by washing up to 10 times with 2 ml H_2O. Thereafter, the orange sample was dried in a vacuum of 10^{-5} bar at 110 °C for 1 h. The chemical analysis (Mikroanalytisches Labor Pascher, Remagen, Germany) yields a ratio of Si:H:O = 6:5.6(1):3.0(1) normalized to six Si atoms, very close to the composition of the ideal composition $[Si_6H_3(OH)_3]_n$. Traces of Cl, found in the chemical analysis, are due to physically adsorbed impurities on the surface of the platelets.

For the preparation of layered polysilane part of the freshly prepared Wöhler siloxene was washed with water and rinsed twice with aqueous HF at 0 °C (5 ml 10% HF in H_2O). Thereafter, the greenish-yellow samples were filtered, washed with 5 ml H_2O and then dried in a vacuum of 10^{-5} bar at 120–130 °C for 1 h. The preparation was performed in a darkened room. The chemical analysis of the layered polysilane yields a ratio of Si:H:O = 6:6.5(1):0.85(1), which indicates a low content of OH groups in the layered structure $[Si_6H_{5.65}(OH)_{0.85}]$.

The as-prepared Wöhler siloxene and the layered polysilane were annealed in vacuum (10^{-5} bar) for 30 min at temperatures in the range from 120–350 °C. The changes in the chemical and optical properties were studied. At 200 °C H_2 gas starts to evolve and the chemical composition changes. The chemical analysis of a Wöhler sample annealed at 350 °C for 2.5 h yields a Si:O:H ratio of 2:0.95(1):0.73(1). Annealing of the siloxenes in oxygen gas was studied in Ref. 20 and leads to SiO_2 with optical properties different from those of the vacuum annealed samples.

All samples were stored in ampoules, which were sealed under inert gas conditions to avoid oxidation in air. The optical measurements were performed with the samples in the ampoules.

B. X-ray measurements

For powder diffraction, the samples were mechanically grinded to avoid texture and preferred orientation. The dry powder was filled into a 0.2 mm glass capillary and sealed under inert gas conditions. The powder diagrams were recorded using $CuK\alpha$ radiation and Bragg Brentano geometry (STOE powder diffractometer).

Layered compounds, like the siloxenes, experience by the grinding a shift of the individual layers leading to a large amount of stacking faults (turbostatic disorder). In general, powder diagrams have to be corrected for the disorder introduced during sample preparation.[21] The corrections are well
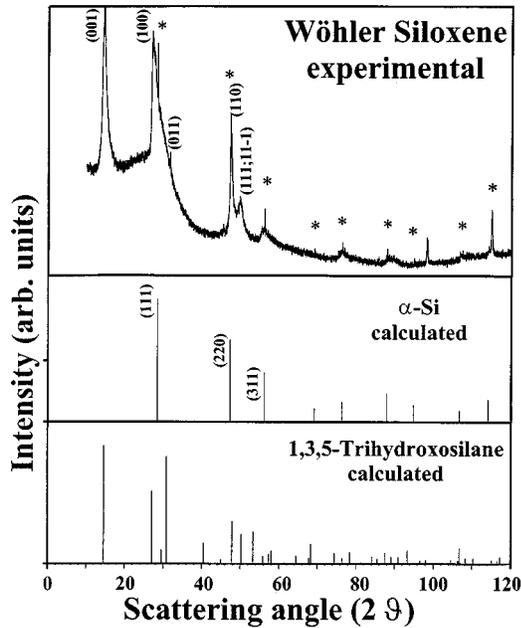
FIG. 2. Powder diagram of Wöhler siloxene (top) and calculated Bragg reflections using data from Table I (bottom). The position of the reflections from α-Si are given in the center. In the top diagram we have marked the reflections from α-Si by *.

C. Optical measurements

All samples synthesized in this study were characterized by their infrared (IR) transmission and photoluminescence (PL) spectra at room temperature. Usually, if not otherwise noted, the samples are at normal pressure in a quartz ampoule under inert gas (Ar) during the PL measurements. Excitation for the photoluminescence measurements is by the 325 nm line of an He-Cd laser, the excitation power is 4 mW/cm^2. The emission spectra were dispersed by a SPEX monochromator ($f = 0.75$ m) and detected by a cooled GaAs photomultiplier with a cutoff wavelength at 900 nm. Simple photoncounting was used to record the data. All spectra presented were properly corrected for the sensitivity of the PL set up. The IR transmission was determined by a Brucker IFS 66 Fourierspectrometer. Small amounts of powdered samples (≈ 1 mg) and dry KBr (300 mg) had to be pressed into pellets within the glove box for the IR measurements.

known but involve some ambiguity. Therefore, for layered compounds a precise structural analysis is achieved only from single-crystal studies. Small crystalline platelets were selected and mounted in a glove box with baked-out silicon grease into a small capillary, which was sealed under Ar atmosphere. The handling had to be performed with great care, because the platelets are sensitive to mechanical stress, which would lead to a distortion of the layered material. Orientation photographs of the $hk0$ and $h0l$ orientations were taken with the precession method using MoKα radiation. Intensities at 20 °C were collected either via an image plate diffractometer (Stoe IPDS, Stoe & Cie., Darmstadt) or a four-circle diffractometer (Stoe STADI 4, Stoe & Cie., Darmstadt).

FIG. 3. Powder diagram of (a) Wöhler siloxene prepared from the TR6 modification of CaSi$_2$ and of (b) layered polysilane.

III. RESULTS

A. Powder diagram

A powder pattern of a freshly prepared Wöhler siloxene sample is given in the top part of Fig. 2. Several Bragg reflections due to siloxene and crystalline Si (α-Si) can be identified. The assignment of the different peaks is according to the structural analysis of siloxene presented below as well as to the known reflections from α-Si. The intensities of the reflections from 1,3,5-trihydroxosilane were calculated for an ideal powder and neglect the effects of the layered structure. Therefore, a direct comparison of the measured and calculated intensities shown in the upper and lower part of Fig. 2 is not possible. The (001) Bragg reflection at 14.2° from siloxene exhibits an observed full width at half maximum (FWHM) of $\leqslant 0.6°$, which is remarkably smaller compared to the reflections observed by Dahn and co-workers[12,13] (2.8°). The reduced width of the peaks in our samples indicates a better crystallinity of the stacked layers and a more homogeneous composition in our samples.

The intensity ratio of the doublet structure at 47° [the (110) and (111) reflections] from siloxene was interpreted by Dahn *et al.* as due to a preferential stacking of the Si layers.[12] In their samples almost 40% of the layers are stacked randomly. A stacking sequence with only 20% of the layers stacked randomly would fit our doublet structure nicely.

The powder diffraction pattern exhibits a broad structured background at small scattering angles. We have not attempted to fit the background properly, as was reported in Ref. 12. Our experience with these fitting procedures is that one should be very cautious with the determined structural details. In the following we will present the powder patterns without subtraction of the background.

We observe in almost all our siloxene powder patterns traces of crystalline α-Si in concentrations up to 1%. In the powder pattern shown in the top of Fig. 2 we have indicated the possible reflections from the small α-Si crystallites. These traces are already present in the educt CaSi$_2$. There is, however, the possibility that in the course of the preparation α-Si is produced through the formation of Si-Si bonds. These reactions are well known from the Zintl phases KSi (Ref. 22) and Li$_3$NaSi$_6$ (Ref. 23). We therefore used for starting material only the modification TR6 of CaSi$_2$, which was free of α-Si crystallites. The Wöhler siloxene from this
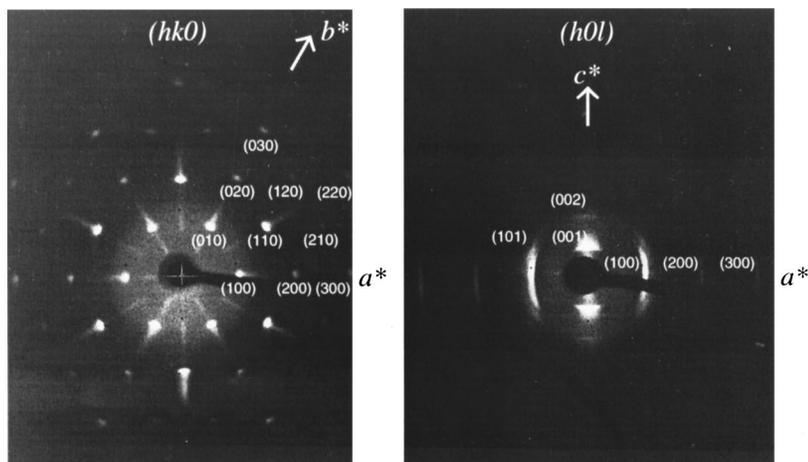
FIG. 4. Top: Precession photographs (MoKα; 3h) with ($hk0$) and ($h0l$) reflexes. a^*,b^*,c^* are the reciprocal lattice vectors. Bottom: Crystal structure of 2D-poly[1,3,5-trihydroxocyclo-hexasilane] with the three disordered sites of the hydroxyl proton.
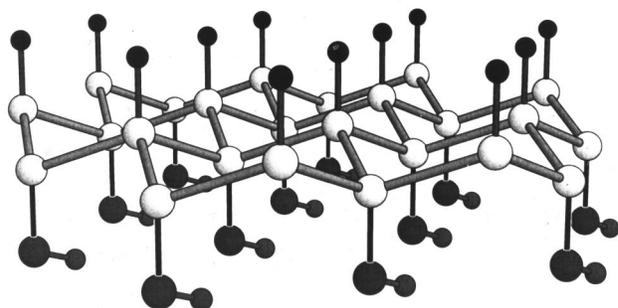
material shows also no contamination due to the α-Si. A typical powder diffraction pattern is shown in Fig. 3 (upper part). The position of the Bragg reflections are identical to those presented in Fig. 2. The sharpness of the reflections and the resolved separation of the (110) and (111) reflections indicates again an almost ideal stacking of the layers.

In Fig. 3 (lower curve) the diffraction pattern of layered polysilane is shown. The positions of the reflections are identical to those of Wöhler siloxene except for the peak at 15.9°, which is due to the Bragg reflections from the planar Si layers. The separation between the layers shrinks in polysilane compared to Wöhler siloxene (see Table II).

Annealing the as prepared Wöhler siloxene in vacuum at around 300 °C slowly destroys the planar structure. Our results are similar to the data presented in Ref. 11. No shift of the layer separation is observed after the annealing steps.

The oxidation of the Wöhler siloxenes at room temperature up to 200 °C was studied in Ref. 20. Already at room temperature the oxidation destroys the planar structure and leads to a smeared out x-ray-diffraction pattern.

B. Single-crystal x-ray investigation

Orientation photographs of the $hk0$ and $h0l$ layer are shown in the upper part of Fig. 4. The single crystal reflections of a layered structure are clearly visible. The diffraction patterns were analyzed and corrected by standard methods used in the x-ray analysis of single crystals. For the $hk0$ projection a total of 18 reflections was used for the refinement with the SHELX program.[24] The refinement converged at $R=0.083$, yielding the positions for the atoms except hydrogen.

The x-ray single-crystal analysis identifies the Wöhler siloxene as a 2D-poly[1,3,5-trihodroxocyclohexasilane]. Table I summarizes all crystallographic details of this structure. The single-bond distance d(Si-Si) for the fourfold-coordinated Si is found to be 234 pm, which is similar to the bond length in α-Si, d(Si-Si)=235.2 pm.[25] The distance is somewhat larger in organosubstituted polysilanes and depends on the nature of the substituent.[24] In silicides with more electropositive elements these distances are larger, because Coulomb interactions and the cations influence the bond length. In most materials the values for the Si-H bond length scatter between 130 and 155 pm, we derive a value d(Si-H)=154 pm for the Wöhler siloxene. The angle Si-O-H is found to be 115°.

The observed symmetry for the $hk0$ projection is trigonal, however, this is not in agreement with the highest possible symmetry of the individual silane layer. Taking the orienta-

TABLE I. Crystallographic details of $^2_\infty$[Poly-1,3,5-Trihydroxocyclohexasilane], ideal spacegroup $P3m1$ (Nr. 156); Z=1/3 Si$_6$H$_3$(OH)$_3$; $a=380$ pm; $c=604$ pm; common U=225 pm^2; 18 $hk0$; $R=0.083$.

Atom	Site	x	y	z^*
Si(1)	1b	1/3	2/3	0
O(1)	1b	1/3	2/3	-0.2650
1/3 H(1)[a]	3d	0.1956	$-x$	-0.3350
Si(2)	1c	2/3	1/3	0.1350
H(2)[a]	1c	2/3	1/3	0.3900

[a]z parameters and proton positions not yet refined.
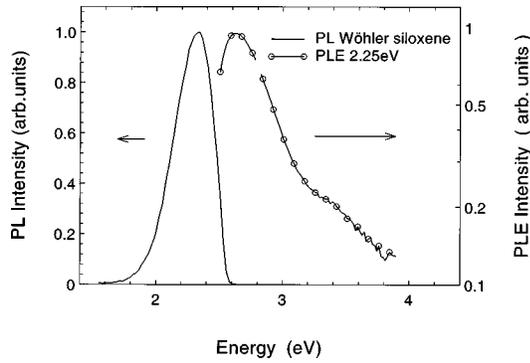
FIG. 5. Photoluminescence and photoluminescence excitation spectra of as prepared Wöhler siloxene. Detection energy for the PLE spectrum was 2.25 eV.

tion of the hydroxyl proton into account, the symmetry of a layer should be orthorhombic *mmm*. The observation of trigonal symmetry can be explained by a static or dynamic disorder or by the formation of twins (a so-called ''Drilling'').

C. Optical properties of siloxenes

1. Wöhler siloxene

The room-temperature PL spectrum of an as-prepared Wöhler siloxene sample has a maximum at 2.30 eV and a FWHM of 300 meV (Fig. 5). The PL spectrum is asymmetric with a low-energy tail. The external quantum efficiency determined from a powdered sample is 10%. The PLE curve detected at the maximum of the PL peak shows a pronounced maximum at 2.6 eV. The onset of the PLE spectrum is around 2 eV. The sharp maximum of the PLE indicates a direct excitonic transition at 2.6–2.7 eV in the planar structure of Wöhler siloxene. Efficient excitation of the green PL is achieved with laser energies in this energy region. The results on the present samples are very similar to those presented in Ref. 26 although, due to the better sample quality the spectral positions of the PL and PLE maxima and the associated linewidth are slightly different.

The Wöhler siloxene sample prepared from the TR6 modification of $CaSi_2$, which contained no crystalline Si contamination, exhibits the same strong PL band at the same energy position. The PLE of the powder is also very similar to the spectrum given in Fig. 5. The argument given by Pinizzotto *et al.*[27] that Si nanocrystals in the siloxene samples are responsible for the strong visible PL of siloxene is therefore not supported by experiment.

The IR transmission of Wöhler siloxene shown in Fig. 6 exhibits characteristic vibrational modes:[28] The Si-H stretching mode at 2100 cm^{-1}, a broad O-H stretching mode at around 3400–3600 cm^{-1} and a mode at 520 cm^{-1}, which was tentatively assigned to a Si-Si vibration of the Si plane. The later mode at 520 cm^{-1} is always observed in samples that exhibit the planar structure in x-ray diffraction. A detailed analysis of the 520 cm^{-1} mode in deuterated Wöhler siloxene is under way and will be published elsewhere.[29]

In addition to the characteristic modes from the ideal Wöhler siloxene structure, modes due to the imperfect structure of our siloxene samples show up, e.g., the Si-O-Si
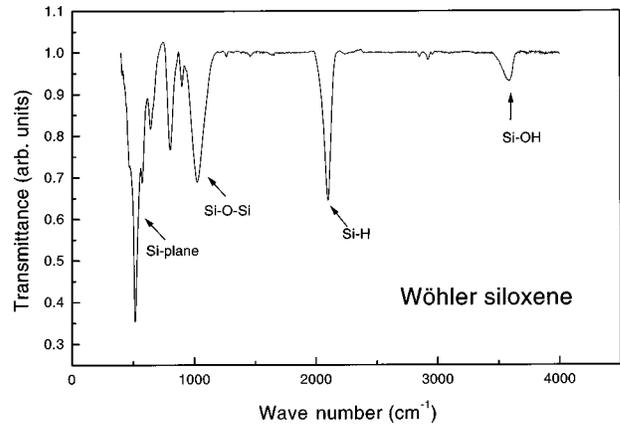
FIG. 6. Infrared absorption spectrum of as prepared Wöhler siloxene.

stretching mode at 1050 cm^{-1} of oxygen atoms bonded to two Si atoms either in the planes or connecting the planes. Weak absorptions at 1400, 2300, and 2900 cm^{-1} are due to different CO_2, CH, and HCl vibrations, where C and Cl are residuals from the sample preparation.

2. Layered polysilane

In the upper part of Fig. 7(a) the PL spectrum of a polysilane sample is shown. The PL maximum is at 2.30 eV and the FWHM is 660 meV. The FWHM is very large compared to that of Wöhler siloxene. We find, however, for some of the polysilane samples a much smaller FWHM of ≈400 meV. At the moment it is not clear which preparation step is responsible for the varying linewidth. For comparison, the PL spectrum of a Wöhler siloxene powder is included in Fig. 7(b). This material was dried after preparation in a vacuum for 14 h at room temperature. Part of the powder was used
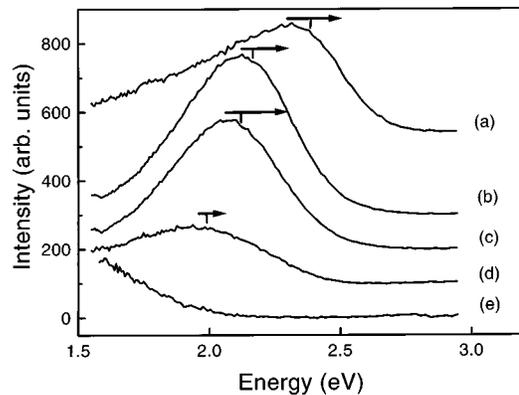
FIG. 7. Photoluminescence spectra from different siloxene samples: (a) polysilane; (b) Wöhler siloxene, as prepared, annealed at RT in a vacuum for 14 h; (c) same as (a) but with an additional 2 h anneal at 120 °C in vacuum; (d) same as (b) but with an additional 30 min anneal at 300 °C in vacuum ; (e) same as (b) but with an additional 30 min anneal at 350 °C in vacuum. All samples were stored in vacuum during the measurements. The arrows indicate the shifts of the spectra after breaking the vacuum with Ar under normal pressure. The length of the arrow indicates the shift measured several days after breaking the vacuum. The marks on the arrows indicate the shifts measured after 2 h of breaking the vacuum. For better clarity we shifted the spectra vertically.
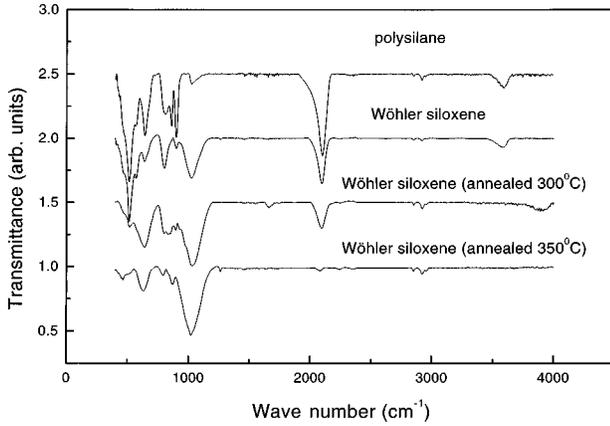
FIG. 8. Infrared transmission from different siloxene samples: (a) polysilane; (b) Wöhler siloxene, as prepared, annealed at RT in a vacuum for 14 h; (c) same as (b) but with an additional 30 min anneal at 300 °C in vacuum; (d) same as (b) but with an additional 30 min anneal at 350 °C in vacuum. The spectra were shifted vertically for better clarity.

for the preparation of the polysilane powder. Spectrum (c) is also from the as-prepared Wöhler siloxene powder, which was, in addition, annealed in vacuum for 2 h at 120 °C, a standard procedure in our preparation to reduce the time of drying the samples. The PL spectra of both Wöhler siloxene powders in Figs. 7(b) and 7(c) are very similar but redshifted compared to the spectrum shown in Fig. 5.

We have tracked down the origin of the different spectral positions of the otherwise identical samples (same preparation, same chemical composition, same x-ray-diffraction pattern, same IR transmission) to the different ambients of the samples during the measurements. In Fig. 5 the sample was as usual kept in a quartz ampoule under Ar gas at normal pressure to avoid the oxidation of the siloxene sample. The spectra shown in Fig. 7 belong to a series of samples where we studied the annealing properties under vacuum. All spectra shown in Fig. 7 are, therefore, from samples that were stored and measured in the quartz ampoules under vacuum. After opening the ampoules under inert gas, the PL spectra show immediately a blueshift, which after several days brings the spectral position back to that of the samples which were never stored in vacuum. We indicate in Fig. 7 the spectral shift of the PL maxima after opening the ampoule by arrows. The final position is only reached after several days, whereas the mark on the arrow indicates the spectral position 2 h after opening of the ampoules. Polysilane and as-prepared Wöhler siloxene show almost the same total shift of 200 meV. There is also an increase in PL intensity after breaking the vacuum. For most samples we measure a factor of 2–3 increase in intensity.

The infrared transmission of layered polysilane below 900 cm^{-1} is quite different from that of Wöhler siloxene [Figs. 8(a) and 8(b)]. Vibrational modes due to oxygen are drastically reduced. The modes of Si-H and the vibration of the Si plane are dominant. Two additional modes around 850 and 890 cm^{-1} are due to Si-H$_2$ vibrations. The two modes correspond to the 845 cm^{-1} scissor wagging mode and the 890 cm^{-1} bending mode of polymerized silicon dihydride in a-Si:H.[30]

3. Heat-treated Wöhler siloxene

The optical properties of Wöhler siloxene are changed by thermal annealing in vacuum. Our results are similar to those reported in Ref. 31, although the details of the spectra are different. The annealing was performed in a vacuum at temperatures up to 350 °C. The color of the samples changes from yellow to brown with annealing at 300 °C for 30 min. The change in the PL spectra is shown in Figs. 7(d) and 7(e). Heat treatments at around 300 °C lead to pronounced shifts of the PL band towards smaller energies. Annealing Wöhler siloxene at 350° C for 30 min results in the largest shift. The maximum of the PL is at 1.4 eV under these annealing conditions [see Fig. 7(e), maximum not shown due to the cut off of the GaAs photomultipilier used]. By varying the annealing conditions (temperature and time) we are able to shift the max of the PL band from 2.1 to 1.4 eV. The intensity of the PL band decreases with the annealing. Above $T \geqslant 400$ °C we could not observe any PL (down to 1 eV).

There is only a small change in the position of the PL maximum in the annealed samples after breaking the vacuum of the quartz ampoule containing the samples, but the PL intensity increases when the samples are measured under normal pressure.

The IR transmission of the vacuum annealed samples reflects the destruction of the planar siloxene structure Figs. 6(c) and 6(d). The mode at 520 cm^{-1} of the Si planes diminishes and the oxygen vibration, characteristic for a three-dimensional bonding increases with annealing. Hydrogen-related modes decrease in intensity with annealing time, in agreement with the reduced hydrogen concentration in these samples. Our results are very similar to those reported by Ubara et al.[11]

During annealing at around 300 °C the PLE spectra change drastically. The excitonic peak at 2.6 eV disappears, and an exponential increase, similar to the Urbach tail[32] in disordered semiconductors, appears. The optical gap is reduced with the annealing.

IV. DISCUSSION

A. Structural details

The crystal structure of Wöhler siloxene develops from the two-dimensional planar Si layer ($^2_\infty$[Si$^-$]) with −H and −OH ligands. The structure of 1,3,5-trihydroxo-cyclohexasilane is in agreement with the observed chemical analysis and spectroscopic data. In the lower part of Fig. 4 we present a schematic model of the planar structure derived from the single-crystal x-ray analysis. The three disordered sites of the hydroxyl proton are schematically indicated. The silicon skeleton is analogous to that of individual layers of gray arsenic.

In Table II we compare the lattice constants of different silane derivates with those of α-Si and CaSi$_2$. The lattice parameters for Wöhler siloxene are derived from the single-crystal analysis whereas the parameters for the layered polysilane originates from the analysis of the x-ray powder pattern. The error in the determination of the lattice parameters are ± 1 pm for Wöhler siloxene and ± 3 pm for polysilane. All compounds listed in Table II exhibit a very similar a axis, indicating identical Si-Si arrangements, their c axes,

TABLE II. Comparison of lattice parameters for different silane derivatives. a gives the length of the unit cells (trigonal setting) for a single silicon layer. The length c gives either the distance between layers or the bond length $d(\text{Si-Si})$ in the case of α-Si.

Compound	a [pm]	c [pm]	Ref.
$Si_6H_3(OH)_3$	380	604	This work (expt.)
Si_6H_6	383	557	This work (expt.)
$Si_6H_3(OH)_3$	383	633–703	[9] (expt.)
$Si_6H_3(OH)_3$		623	[11] (expt.)
$Si_6H_3(OH)_3$	383	590	[12,13] (expt.)
$Si_6H_3(OH)_3$	383	532	[6] (calc.)
Si_6H_6	383	540	[12] (expt.)
Si_6H_6	383	478	[6] (calc.)
$CaSi_2$ (TR3)$(c/3)$	382.0	532.7	[17] (expt.)
$CaSi_2$ (TR6)$(c/6)$	385.5	510.7	[19] (expt.)
α-Si$(a_0 = 543.102$ pm$)$	384.0	235.2	[25] (expt.)

however, differ substantially depending on the nature of the substituents and/or the method of preparation. The relatively long c axis reported by Weiss, Beil, and Meyer[9] might indicate a higher $-$OH content in their compound. The calculations by Van de Walle and Northrup[6] reveal a layer separation of only 532 pm, again quite different from the experimentally determined 604 pm in our Wöhler siloxene. Layered polysilane exhibits the same in-plane lattice constant but a smaller separation of the planes.

The three-dimensional precession x-ray data need further analysis, to determine possible short-range ordering effects of the layers. In a number of experiments we have observed additional superstructure reflections which result from a threefold c axis. In addition a careful analysis of the intensity distribution of the reflections is under way which will allow us to determine the ordering of the layers.

B. Optical properties

The electronic band gap of the planar siloxene structure shown in Fig. 1(a), which is terminated by OH and H groups, was calculated with different methods. Déak *et al.* obtain with semiempirical methods a band gap energy of 2.7 eV. Van de Walle and Northrup[6] and Takeda and Shiraishi[33] used density functional methods and obtained a direct band structure with a band gap of 1.7 eV. These calculated values should be compared to our measurements, where a maximum of the PL is found at 2.3 eV and the maximum for the PLE is at 2.7 eV.

The electronic structure of layered polysilane was first studied by Takeda and Shiraishi.[34] An indirect gap at 2.48 eV and a nearby direct gap at 2.63 eV were calculated. A similar behavior, with somewhat larger gap energies (indirect gap at 2.75 eV, direct gap at 2.95 eV) was determined by Van de Walle and Northrup.[6] First experimental evidence for layered polysilane was presented by Dahn *et al.*[12] We have performed a PL study on this material. The maximum of the strong PL is found at 2.5 eV and the maximum of the PLE spectrum is at 2.7 eV, in good agreement with the theoretical predictions. From the strong PL intensity it is difficult to attribute the PL to an indirect optical transition.

During thermal anneal in vacuum at around 300 °C the two-dimensional planar structure is destroyed by oxygen insertion and cross linking. The band gap shrinks from 2.7 to 1.9 eV as is evidenced by the onset of the PL spectra. Hydrogen is lost from the compound but the Si:O ratio of 2:1 remains constant.

Oxidation of Wöhler siloxene leads already at room temperature to a destruction of the planar structure.[20]. The PL shifts first with oxidation to smaller energies (from 2.3 to 2.0 eV) but with increasing oxidation the PL is blueshifted (up to 2.4 eV). The composition of the Wöhler siloxene changes with oxidation to a substoichiometric hydroxide with Si:O:H ratio equal to 1:1.5:1.

The change of the PL spectral position and intensity with the ambient in our annealing studies shows the strong influence of adsorbed molecules between the layers of the planar structure. Pressure effects which change the bonding length or angles can be excluded. The blue shift of 200 meV from vacuum to normal air pressure is much larger and in opposite direction to that expected from hydrostatic pressure measurements on Wöhler siloxene.[35] No changes of the x-ray reflections were observed after opening the evacuated ampoules.

C. Wöhler siloxene versus porous silicon

As prepared Wöhler siloxene is usually wrongly referenced as the material responsible for the strong PL in porous Si. As we have shown in this study, the position of the PL maximum for this compound is well in the green (2.3 eV), whereas the strong RT PL in porous Si exhibits a maximum in the red (1.8 eV). Brandt *et al.*[2] proposed that as-prepared siloxene samples had to be heat treated in oxygen atmosphere below 400 °C, to shift the PL maximum from green to the red color of porous silicon. During oxidation the oxygen was believed to switch into the Si plane and a change from structure a to c shown in Fig. 1 takes place. In our recent study[20] we could indeed show that the PL of Wöhler siloxene shifts under slow oxidation towards the red with max at 2.0 eV, but further oxidation leads to a pronounced blue shift. Under no experimental conditions of oxidation it was possible to reach a maximum of the PL at 1.8 eV. The chemical composition changes under oxidation to SiO_x, with x close to 2.

In the present study, we are able to shift the maximum of the PL from 2.3 to 1.4 eV, by annealing of Wöhler siloxene in vacuum at temperatures around 300 °C. The composition of the samples changes again to SiO_x, but with x close to 0.5. During the annealing the oxygen from the OH ligands is incorporated into the ideal Si planes of Wöhler siloxene and destroys the planar structure. Calculations by Pederson *et al.*[7] indicate that bridging oxygen between Si atoms leads to an energetically favorable structure. We can speculate that one dominant building unit could be the sixfold Si ring, which is isolated by bridging oxygen from other rings. We agree with Dahn *et al.*[12] that the ideal structure shown in Fig. 1(c) which was proposed by Kautsky[10] and emphasized by Brandt *et al.*[2] is not realized in the vacuum annealed Wöhler siloxene. We recently successfully prepared siloxene that seems to have the structural properties shown in Fig. 1(c). The optical properties of this material are, however, different from those found for the Wöhler siloxene. Details of this study will be presented in a forthcoming publication.

Our IR transmission, PL and PLE spectra of vacuum annealed Wöhler siloxene are very similar to those reported in Refs. 2 and 28 and we believe the annealing conditions used there (pressed powder in ampoules were heated in air) correspond better to an anneal in vacuum than an oxidation process. The optical properties of the vacuum annealed Wöhler siloxene are very similar to those found in porous Si, which exhibits the strong red RT PL. Therefore the proposal made in Ref. 2 that siloxene derivatives generated from as prepared siloxene by annealing should be seriously discussed in the light of recent publications.

The K- and L-edge x-ray absorption of porous Si, as-prepared siloxene, and layered polysilane show remarkable similarities.[13] Based on the argument given in Refs. 16 and 36, that porous Si can be predominantly oxygen free, Dahn and co-workers discard the possibility of siloxene in the porous Si layers and propose that porous Si may consist out of polysilane (Si_6H_6) layers. However, as we have shown in this study the PL maximum of layered polysilane is at 2.5 eV, far off from the position of the strong PL in porous Si. There are also several publications that question the direct involvement of hydrogen in the PL layers of porous Si. From a combined study of the IR transmission and PL on porous Si no correlation between the hydrogen vibrational modes and the PL spectra could be established[37,38] and an involvement of polysilane in the strong PL from porous Si has to be denied.

The chemical composition of porous silicon was determined by several different methods. Infrared absorption of freshly prepared porous silicon showed no oxygen-related vibrational modes.[39] Although the authors give no PL spectra of their as-prepared material they emphasize that the maximum of the PL is similar to that reported by Brandt et $al.$[2] The lack of oxygen in porous Si is for the authors strong evidence that siloxene $Si_6H_3(OH)_3$ is not responsible for the PL in porous Si. We find a close resemblance of the IR spectra given by Tischler et $al.$[39] for porous Si with the spectrum shown in Fig. 8 for polysilane. Under certain conditions we find in as prepared porous Si samples a very similar IR spectrum but the PL spectrum shows in this case a maximum at around 2.3–2.5 eV.

The chemical composition of porous Si samples that exhibit a PL max at 1.45 eV were determined by several authors. Canham et $al.$[40] use a SIMS analysis to determine O, H, Si, and C concentrations. Interesting changes in the composition of porous Si layers were detected with storage time in air. However, the determination of absolute and relative concentrations by SIMS is very difficult due to the complicated matrix of porous Si. Alternative ion beam techniques that determine the composition are used in Ref. 41. A relative composition was determined as $Si_{2.5}O_{1.2}C_{1.3}H_{1.2}$, very close to the composition of annealed Wöhler siloxene Si_2O_1, which exhibits a PL max at 1.5 eV.

Selective excitation of the PL spectra at the absorption of the Si core levels with synchrotron radiation is a very selective tool to determine the chemical environment of the Si atom. Sham et $al.$[15] compare differently prepared siloxene and porous Si samples and from their data they conclude that the PL in porous Si is not of the same origin as that in as-prepared siloxene, polysilane or thermally annealed siloxene. However, the PL of their samples (porous Si max at ≈ 750 nm, freshly prepared siloxene max at ≈ 520 nm, and annealed siloxene max at ≈ 540 nm) clearly indicates a wrong preparation of the annealed siloxene samples. Apparently, Sham et $al.$ annealed at 400° without specifying the ambient. From our oxidation study[20] we believe that an oxygen-rich compound was formed, which certainly should not be identified with porous Si.

A characteristic feature of porous silicon is the polarization memory effect of the PL.[42–44] We have preliminary results on a very similar effect in our Wöhler siloxene samples. Annealed Wöhler siloxene exhibits polarization degrees comparable to porous silicon. Crystalline Wöhler siloxene however shows a pronounced polarization only if the exciting laser is polarized parallel to the c axis of the layers. A detailed investigation is underway and will be published elsewhere.

There were several proposals to explain the optical properties of porous silicon by a combination of nanocrystals and surface layers (like SiO_2) or surface states (like specific molecules). Bridging of nanocrystals by oligosilane bridges was proposed, and the optical properties were attributed to excitations in the bridging molecules (see the discussion in Ref. 3). All these models require both constituents, nanocrystals and surface states or molecules to account for the optical properties in porous silicon. The nanocrystals are necessary to model the absorption properties of the excitation light, whereas the visible PL (in the red) originates in the surface layers of the nanocrystals. The siloxene derivates discussed in this paper can be identified with the species on the surface of the nanocrystals. However, in pure siloxene layers prepared from $CaSi_2$ no nanocrystals are needed to account for their optical properties.

V. SUMMARY

We have studied the fascinating optical properties of layered silicon planes in Wöhler siloxene and polysilane. The strong PL at RT can be tuned from 2.5 to 1.4 eV by heating the samples in vacuum. We have prepared single crystalline siloxene and polysilane samples and have identified their structural properties. The thermal anneal leads to a destructrion of the Si planes, which is evidenced by changes in the x-ray diffraction and the infrared spectra. We discuss recent publications on the origin of the strong PL in porous Si and support the arguments that vacuum annealed Wöhler siloxene is responsible for the strong PL in porous Si.

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