VISIBLE LUMINESCENCE FROM SILICON: QUANTUM CONFINEMENT OR SILOXENE ?

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ABSTRACT

The discovery of strong visible photoluminescence at room temperature from porous silicon has triggered new hope that light-emitting devices compatible with existing Si–technology might become possible. We first review the luminescence behavior observed in silicon-based materials such as amorphous Si, microcrystalline Si, or SiO_2. We then critically discuss the present model for the luminescence from porous silicon based on quantum confinement in view of the growing experimental evidence for the importance of both hydrogen and oxygen to obtain efficient luminescence from this material. We propose an alternative explanation based on the presence of siloxene ($Si_6O_3H_6$) in porous silicon which is corroborated by experimental results obtained with photoluminescence, Raman and IR spectroscopy. An important aspect is that siloxene can be prepared by methods different from anodic oxidation, and one particular technique will be described together with possible ways to tune the luminescence energy.

INTRODUCTION

The development of active optoelectronic devices compatible with Si technology has been an important challenge during the last decade. Undoped crystalline silicon (c–Si) with its indirect bandgap shows a weak luminescence at 1.1 eV due to excitonic recombination [1]. This luminescence can be electrically excited in a *pn*-diode when operated in breakdown at high reverse bias voltages, still the external quantum efficiency, η, is well below 10^{-5} [2]. Various possibilities to achieve stronger luminescence have been explored, and some of the results are given in Table 1 which summarizes the spectral positions and the approximate room temperature efficiencies of the observed luminescence.

A possible approach has been the introduction of specific luminescence centers in crystalline silicon. This has been shown for carbon implanted samples which, after electron irradiation, exhibit a strong electroluminescence at 0.95 eV [7]. At 77 K, the luminescence intensity is comparable to that of N-doped GaP, also an indirect band gap material which is used for commercial fabrication of green light emitting diodes. Unfortunately, the luminescence in C–doped Si has not been observed at higher temperatures. In erbium implanted Si, the characteristic intraatomic transition of Er^{3+}-ions is observed at ≈ 0.8 eV [8]. This luminescence, which would be suitable for silica-fiber-based optical communication systems, however, disappears at temperatures above 200 K.

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Material	Mechanism/Preparation	Position (300 K)	η (300 K)	EL	Refs.
c-Si	exciton, electron-hole-liquid	1.1 eV	10^{-6}	*	[1,2,3]
	Auger	2.2 eV	$\approx 10^{-16}$	*	[4,5]
	luminescence centers	0.49 – 1.15 eV			[6]
	C implanted	0.95 eV	10^{-2} ($\leq$77 K)	*	[7]
	Er implanted	0.8 eV	(<200 K)		[8]
μc-Si	rf sputtered	2 eV			[9]
	in SiO_2-matrix	2 eV		*	[10]
	post-hydrogenated	1.0 eV	10^{-6}		[11,12]
polysilane	organo-substituted	3.1 – 3.7 eV			[13,14]
	in liquid solution		30%		
	in solid matrix		10^{-4}		
	higher-dimensional polymer-networks	2.7 eV	10^{-5}		[15,16]
	a-Si:H_x (HOMOCVD)	2.05 eV	1%		[17]
	polysilane alloy with a-Si:H	1.2 – 1.6 eV	10^{-4}		[18]
a-Si:H	recombination at Si dangling bonds	0.9 eV	10^{-5}	*	[19,20]
	surface contamination	2.3 eV			[21]
a-Si:O:H	increase of bandgap by O-alloying	1.0 – 1.6 eV	10^{-5}		[22]
SiO_2	E'-center	2.2 – 2.6 eV			[23,24]
	UV-induced defects	1.9 eV			[25]
	valence-alternation pair	4.0 – 4.5 eV			[26]
	porous SiO_2, contaminated?	1.7 & 2.2 eV			[27]
porous Si	anodic oxidation	1.7 – 2.2 eV	$\leq$10%	*	[28,29]
	stain etches	1.8 eV			[30]
siloxene	Si_6-rings (OH and H terminated)	1.0 – 4.0 eV	10%		[31,32]
cyclosilane	$Si_6(C_6H_5)_x(OH)_{12-x}$	yellow	strong		[33]
Si/Ge SL	quasi-direct (misfit dislocation?)	0.84 eV	10^{-6} (4 K)		[34,35]
GaP	N doped	565 nm	0.3% (EL)	*	[36]

Table 1: Compilation of luminescence data reported for silicon-based materials. The efficiencies, η, at room-temperature are in some cases estimated by the present authors. An asterisk in the column EL indicates that electroluminescence was reported. GaP, the material used in commercial light emitting diodes, is included for comparison.

Another way to circumvent the indirect nature of optical transitions in silicon is the relaxation of the k-selection rule due to spatial confinement in microcrystals. Various preparation methods have been used to generate thin films containing microcrystals, and luminescence in the red and in the infrared has been reported, but again the luminescence efficiencies are extremely small [9,10,11,12]. Localization of carriers can also be achieved in polysilanes. There, thin amorphous polysilane films grown by homogeneous chemical vapor deposition have shown the strongest photoluminescence with an efficiency of about 1% at 300 K [17].

Carrier localization by disorder is the mechanism which gives rise to the strong 1.3 eV luminescence of amorphous silicon (a-Si:H) at temperatures below 100 K [19]. At room temperature, a-Si:H only has a weak luminescence in the infrared, which is attributed to radiative recombination via the dominant defect in this material, the dangling bond. Increasing the bandgap by alloying the silicon with oxygen or carbon shifts this luminescence to the visible range, but the efficiency stays well below 1% (see e.g. [22]).

Radiation due to defect recombination can also be seen from SiO_2. Well known examples are the green luminescence caused by electronic transitions at E' defects and the red luminescence associated with radiation defects [23,25].

With the only exception of the polysilane films produced by HOMOCVD, all these systems still exhibit rather moderate quantum efficiencies. This situation changed drastically, when Canham reported that anodically etched porous silicon (p-Si) shows a strong visible photoluminescence at room temperature [29]. The maximum of the emission is adjustable from the green to the red region of the spectrum, and the efficiency can reach up to 10%. To place this observation in the proper perspective, we compare in Fig. 1 the luminescence spectra obtained from porous silicon to those of some other modifications of silicon discussed above. It is evident that at room-temperature the integrated luminescence efficiency of porous silicon is about four orders of magnitude stronger than of amorphous silicon and about six orders of magnitude stronger than the luminescence from crystalline silicon.

Also included in Fig. 1 is another material, siloxene ($Si_6O_3H_6$), which is the only Si–based compound known in the literature to have a luminescence intensity comparable to that of porous silicon [37]. Siloxene can exist in three different crystalline structures, one of which consists of six-fold silicon rings which are interconnected by oxygen bridges to form a planar arrangement. Photo-excited carriers remain essentially localized in the silicon rings. The optical properties of this material have therefore been compared to those of benzene rings. As in aromatic systems, the luminescence color of siloxene can easily be tuned by changing the ligands of the silicon ring atoms. In this article, we argue that the luminescence in porous silicon is in fact due to certain siloxene derivates formed during the etching process and we will discuss an alternative method to prepare a luminescent layer on silicon.

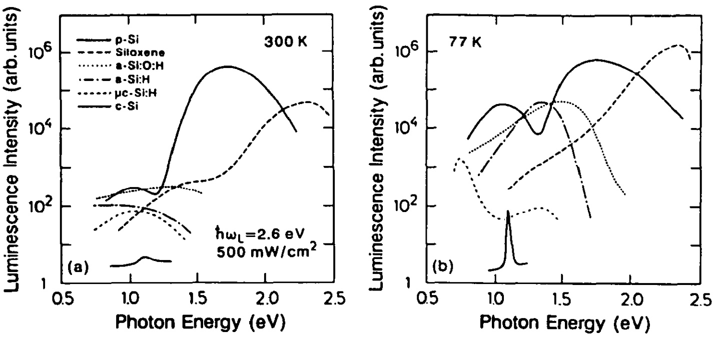

Figure 1: Comparison of the photoluminescence spectra of various silicon based materials at 300 K (a) and at 77 K (b): porous silicon (p-Si), amorphous hydrogenated silicon-oxygen alloy (a-Si:O:H), amorphous hydrogenated silicon (a-Si:H), microcrystalline silicon with hydrogen passivated grain boundaries (μc-Si:H) and crystalline silicon (c-Si). Note that the intensity scale covers six orders of magnitude.

THE ORIGIN OF LUMINESCENCE IN POROUS SILICON

Quantum Confinement

Porous silicon (p-Si) is obtained by anodic oxidation of crystalline silicon. In this technique, a silicon wafer forms the anode of an electrolytic cell, and a mixture of hydrofluoric acid and ethanol is used as the electrolyte. Porous silicon formation occurs at low current densities and high HF concentrations. If these conditions are not met, electropolishing of the silicon surface is observed. Although the formation of a red deposit was already described by Uhlir [38] in his pioneering work on electropolishing, it was only noticed in 1984 that this films exhibit photoluminescence at low temperatures [28]. The room-temperature photoluminescence was discovered even later, in 1990 [29]. More recently, a similar photoluminescence was also reported from "stain films" formed on silicon during etching in $HF:HNO_3:H_2O$ without any current applied [30].

The microscopic structure of a typical porous silicon film is shown in Fig. 2. The film consists of a skeleton of crystalline silicon wires (diameter ≈ 20 nm), with evidence of an amorphous phase filling part of the remaining volume. To date, the standard model for the origin of the luminescence is mainly based on this structural appearance: The spatial confinement of carriers in small crystals is expected to give rise to an increase of the optical transition energies by [39]:

$$\Delta E \approx \frac{3\pi^2\hbar^2}{m^*d^2} - \frac{3e^2}{\epsilon d} ,$$

where m^* is an average effective mass and d is the diameter of the crystallite. The first

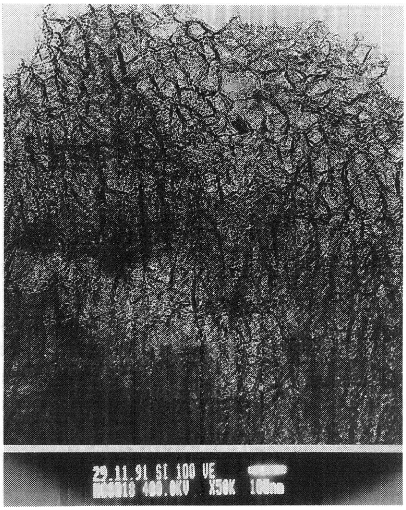

Figure 2: TEM micrograph of a porous silicon layer. The white bar represents a length of 100 nm

term is the actual confinement energy, which is reduced by the Coulomb interaction (second term). Similar arguments apply to confinement in higher dimensions ("quantum wires"). To account for the increase in the optical gap by 0.5 – 1 eV assumed for p-Si, confinement in particles of dimension $d \approx 2$ nm is required. Due to the term $1/d^2$, the energy shift is in fact very sensitive to variations in the diameter d when d becomes small. The rather small width of the luminescence band in porous silicon (0.3 eV) thus calls for a very narrow distribution of the silicon particle diameters, the standard deviation should be less than 0.5 nm. For the quantum confinement model to successfully explain the luminescence from porous silicon with a quantum efficiency reaching 10%, we therefore have to expect that at least 10% of the optically excited volume contain crystallites or Si-wires of the right size and shape. Quantum structures of this size have indeed been observed with high resolution TEM, although generally not in a sufficient quantity and not with a sufficiently narrow size distribution.

Raman spectroscopy is a useful tool to independently evaluate the size of microcrystals in silicon films. The spatial confinement of phonons results in a characteristic softening of the Raman peak due to optical phonons ($\omega = 521$ cm^{-1} for c-Si), together with a corresponding broadening of the line. Fig. 3 shows the correlation between the shift, $\Delta\omega$, and the width, Γ, of the Raman peak for microcrystalline silicon samples with crystallite sizes varying between 3 nm and 50 nm. The theoretical predictions for spherical and cylindrical crystallites (dashed and dotted lines in Fig. 3) describe the experimental behavior satisfactorily (see e.g. [40]). The results for porous silicon ($\Delta\omega \approx 6$ cm^{-1}, $\Gamma \approx 8$ cm^{-1}), however, are incompatible with the known phonon-confinement results. We want to stress that for Raman spectroscopy, freestanding thin films should be used to avoid scattering from the crystalline substrate which would lead to erroneous

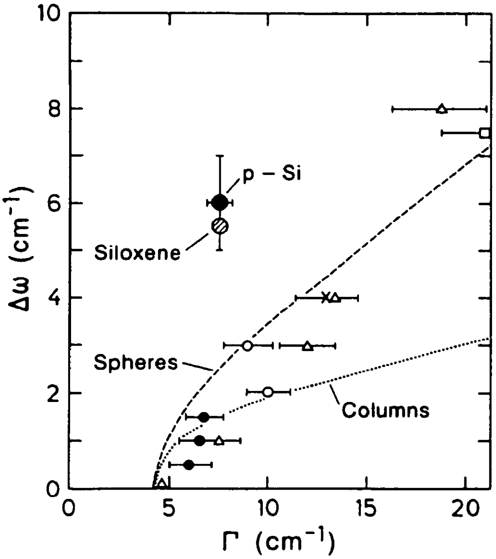

Figure 3: Width Γ of the TO-phonon Raman peak versus shift $\Delta\omega$ from the position in crystalline silicon. Small symbols present experimental data for microcrystalline silicon, large symbols those for porous silicon and for siloxene. Dashed and dotted lines are the theoretical results for spherical and columnar crystallites.

results.

In addition to the discrepancies with the quantum confinement model discussed so far, i.e. the size distribution and number of crystallites as well as the missing evidence for phonon confinement in Raman scattering, there are several other experimental results which are difficult to understand within this model. In particular, the low temperature radiative lifetime is surprisingly long (milliseconds) and, moreover, almost independent of the recombination energy [41]. A further point is the pronounced dependence of the luminescence peak position on excitation energy [42]. Finally, we mention the surprising reproduceability of the luminescence. The same red luminescence centered at around 1.6 – 1.7 eV can be produced under very different etching conditions (current densities, electrolyte composition, doping and orientation of the substrate, etch cell design). implying that very similar size distributions of microcrystals are produced in each case.

Siloxene

When looking for an alternative interpretation of the luminescence, Table 1 shows that, apart from organo-substituted polysilane solutions and polysilane in a-Si:H, only siloxene and its derivates show a luminescence with energy and quantum efficiency comparable to porous silicon. Therefore we will now look more closely at the possibility of siloxene as the origin of the luminescence in porous silicon.

Two different modifications of siloxene are shown in Fig. 4. The first modification consists of corrugated silicon (111) layers (Fig. 4(a)). Ideally, these layers are passivated by alternating H and OH ligands, adding up to the formula $Si_6O_3H_6$. In the second modification, the oxygen atoms have been moved into the silicon planes in such a way

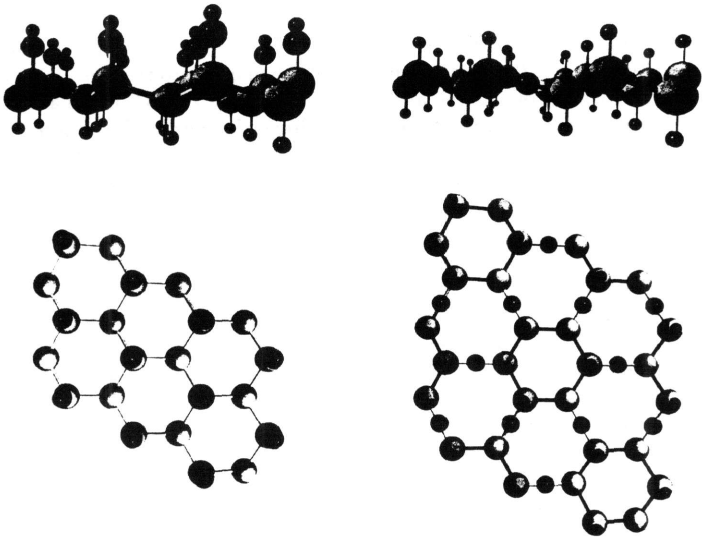

Figure 4: Two structural modifications of siloxene. (a) Si plane, (b) Si_6 ring modification.

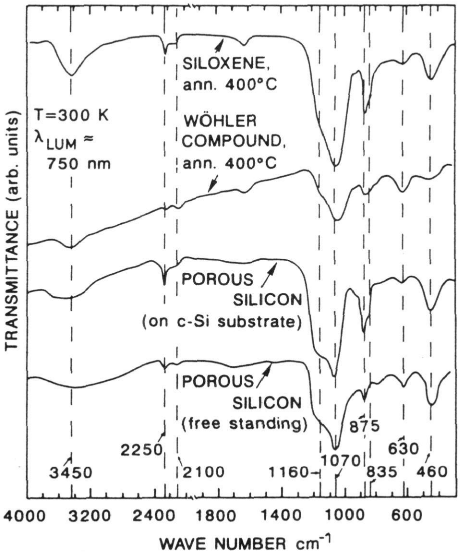

Figure 5: Comparison of the IR transmittance spectra of two porous silicon samples and of two siloxene derivates. All samples show a room temperature luminescence centered around 750 nm and with a high efficiency.

that rings consisting of six silicon atoms (Si_6) are formed which are isolated from each other by oxygen bridges. Here, the fourth valence of the silicon atoms is passivated solely by hydrogen (Fig. 4(b)) [32]. A transformation of the planar into the ring structure can be achieved by annealing of siloxene at temperatures above 200 °C. If the annealing is performed in an oxygen containing atmosphere hydrogen ligands can be replaced by O-H or O-Si, resulting in an additional oxidation. We propose that these partially oxidized siloxene derivates are responsible for the luminescence of porous silicon.

Evidence for this suggestion is for example given by the striking similarities in the infrared transmission spectra of porous silicon and siloxene (Fig. 5). As expected from the structural models in Fig. 4, the siloxene derivates show a number of Si-O, Si-H and O-H vibrational bands, whose assignment has been discussed elsewhere [41]. What is important for the present argument is the fact that porous silicon samples, which exhibit the same strong luminescence also have identical vibrational properties. All bands observed in the siloxene derivates can be found in the porous silicon samples with slight variations in the relative intensities.

The strong similarities between porous silicon and siloxene are not restricted to the vibrational properties. After pulse excitation, both materials show the same slow decay of the photoluminescence with typical lifetimes of the order of milliseconds [41]. Both materials exhibit a pronounced luminescence fatigue which can be reversible as in amorphous silicon, or irreversible when oxygen is present during illumination (photodegradation). Even details of the recombination process as revealed by optically detected magnetic resonance (ODMR) are identical in porous silicon and in partly oxidized siloxene. In both materials one observes a resonant luminescence quenching at a g-value of ≈ 2.005 with a linewidth of approximately 15 G. The quenching ODMR transition in both materials has a characteristic lifetime of the order of a millisecond at 10 K, in good agreement with the result from the time-resolved photoluminescence. The sum of all these similarities strongly suggests that in fact certain siloxene derivates form the luminescent entity in porous silicon. Our identification leads a novel approach to prepare luminescent layers on silicon and to tailor their optical properties.

SILOXENE FILMS ON CRYSTALLINE SILICON

As described in the preceeding section siloxene is a layered structure consisting of silicon (111) planes as the structural backbone. A basic requirement for the preparation of siloxene is therefore to start from a silicon compound already which contains such silicon planes. The best known procedure uses calciumdisilicide, $CaSi_2$, as such a starting material. There are two different recipes for the preparation of siloxene from $CaSi_2$, one going back to Wöhler, who called the substance obtained "Silicon" [31], and one found by Kautsky, who coined the current name "siloxene".[1] According to Kautsky's recipe [32] one inserts $CaSi_2$ for several hours in a cooled mixture of ethanol, water and a small

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[1] Siloxene should not be confounded with siloxane, which is a polymeric compound of the form $(SiH_2\text{-}O\text{-})_n$.

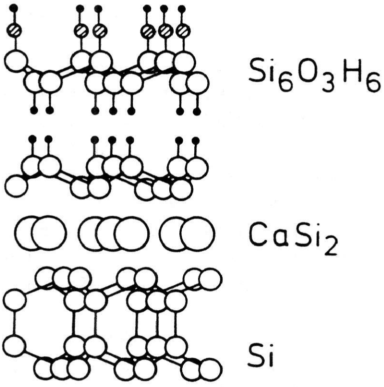

Figure 6: Schematic picture of the formation of siloxene from $CaSi_2$ grown on crystalline silicon.

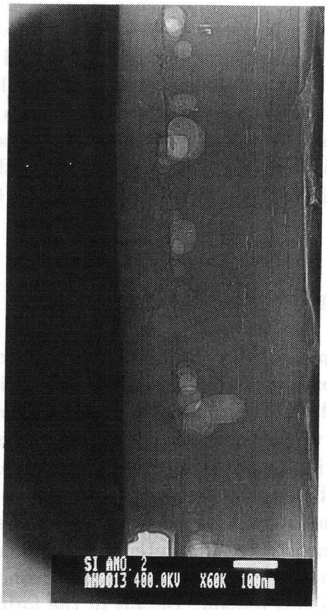

Figure 7: TEM micrograph of a siloxene film obtained by the method described in the text. The film luminesces in the green. The white bar corresponds to a length of 100 nm.

quantity of hydrochloric acid under exclusion of air and light. During this reaction, the calcium is taken out of the solid under formation of $CaCl_2$, the silicon bonds left are then passivated by H- and OH-groups formed by the hydrolysis of the ice water.

X-ray diffraction experiments have shown that in both $CaSi_2$ and in the siloxene modification consisting of the undisturbed silicon planes the lattice mismatch with respect to crystalline silicon is surprisingly small. While the Si (111) planes are slightly enlarged by 0.3% in $CaSi_2$ as compared to c-Si, the siloxene layers have a mismatch of -0.5% [43]. This situation is schematically indicated in Fig. 6, where the crystalline silicon lattice at the bottom, a $CaSi_2$ layer in the middle and the siloxene layer obtained after chemical transformation are shown. These small lattice mismatches should allow the epitaxial growth of both $CaSi_2$ and siloxene on silicon (111) surfaces. For $CaSi_2$ this has indeed been demonstrated [44], whereas the transformation of $CaSi_2$ into an epitaxial layer of siloxene as a second step is currently under investigation. Fig. 7 shows a TEM micrograph of one of the films produced by this method. While porous silicon resembles a sponge of silicon dendrites as seen in Fig. 2, the siloxene film is homogeneous. The striations in the siloxene layer prove that preferential alignment parallel to the Si (111) surface has indeed been achieved. (The origin of the line of "bubbles" seen in Fig. 7 is not clear at the moment, but could be due to calcium precipitates.) Siloxene layers thus prepared commonly show a strong blue/green luminescence similar to bulk siloxene under excitation with the 458 nm line of an Ar^+-ion laser.

The range of luminescence energies which can be obtained from siloxene is surprisingly large. It covers the entire visible spectrum: Blue, green, yellow, red as well as infrared luminescence has been observed in our samples (Fig. 8). In particular, for the Si_6 ring modification of siloxene the luminescence is known to depend strongly on the substitution of the hydrogen ligands by other groups such as halogens, alcohol-, amino- or OH-groups. The strongest effect is observed when OH groups are attached. Unsubstituted $(Si_6O_3)H_6$ luminesces in the blue/green, $(Si_6O_3)H_5(OH)$ in the yellow, $(Si_6O_3)H_3(OH)_3$ in the red and $(Si_6O_3)(OH)_6$ in the infrared region of the spectrum [37].

CONCLUSIONS

The purpose of the present article has been to discuss the origin of the visible luminescence from porous silicon. We have mentioned a number of experimental results which cast doubt on the applicability of the quantum confinement model to this phenomenon. Instead, we propose that a certain class of silicon/oxygen/hydrogen compounds, siloxene and its derivates, forms the structural origin of the visible luminescence in porous silicon. This model suggests alternative preparation methods for luminescent layers on silicon and could have a number of promising application in silicon optoelectronics. We have demonstrated that intense blue, green and red room temperature luminescence can be produced in siloxene layers on silicon. However, a number of unresolved questions and problems remain. Details of the formation of siloxene derivates during the anodic oxidation are not yet clear. Other important aspects which have to be addressed in the

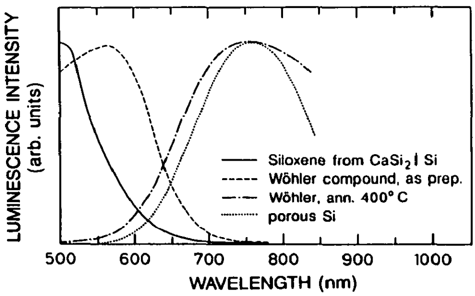

Figure 8: Comparison of the normalized photoluminescence of different siloxene samples and of porous silicon under optical excitation with 458 nm.

future are stability, electrical excitation, limitations imposed by recombination lifetimes, structuring and the precise control of the luminescence energy.

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