

ed to longer wavelengths as was already observed for the corresponding unsubstituted annulenes.^[1,2] It is hoped that unusual modifications of carbon can be constructed from these intermediates after deprotection and renewed coupling of their terminal triple bonds. We hope that the synthesis of further intriguing enediynes will be reported in the near future.

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Light from Silicon—Renaissance of Siloxene and Polysilane?*

By Christian Zybilla* and Vesselinka Petrova-Koch*

In crystalline silicon c-Si radiative recombination processes are only possible in limited amounts (quantum yields of ca. $10^{-4}\%$) as a result of the indirect band gap(s) $E_{g, ind.}$. Since, because $E_{g, ind.} = 1.11$ eV, the luminescence^[1] does not lie in the visible spectral region, this semiconductor, otherwise so frequently used in microelectronics, is not suitable for optoelectronic applications. A solution is offered by the qualitative alteration of the Si band structure during the transfer to nanocrystalline structural units in the “quantum size regime” (i.e. the range in which the size of the particles influences the physical and chemical properties) or by use of luminescent silicon molecular compounds.

The luminescence described here of porous silicon is caused essentially by emission from quantized states in the crystallite interior as well as from energetically low-lying states on the crystallite surface.

Since 1990, the scientific interest on the subject of “light from silicon” has increased exponentially. The reason for this was the observation^[2a] of a red to green photoluminescence from nanoporous silicon, which is even visible to the naked eye at room temperature and has a quantum yield of

several percent. This is comparable with the luminescence from GaAs, the most frequently used material for optoelectronic applications at present.

Thus, the luminescence–quantum yield of porous silicon is five orders of magnitude greater than that of c-Si. (Fig. 1, the scale of the intensity of the photoluminescence extends over six orders of magnitude). Furthermore, it was shown^[2b–d] that the luminescence from the band (ca. 0.3 eV wide) can also be excited electrically; however, the quantum yields of the electroluminescence ($10^{-3}\%$) are still relatively low. Thus, this result can be considered as a first step in the direction of optoelectronic building blocks based on silicon.

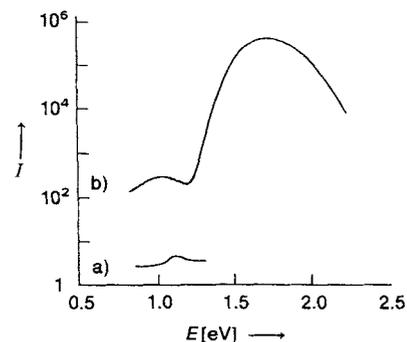


Fig. 1 The photoluminescence spectrum of porous silicon at 300 K (b) compared with that of c-Si (a) [12c]. The intensity I of the luminescence ($I = h\nu = h\omega$ [eV]) extends over six orders of magnitude (Excitation: $h\omega_i = 2.6$ eV = 500 mNcm⁻²).

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Porous silicon is generally prepared by anodic etching of c-Si wafers in HF.^[3] Investigations with transmission electron microscopy (TEM)^[4a] and X-ray diffraction^[4b] show that a self-organized nanostructure is thus formed (for a growth model see [5]). In the case of luminous porous silicon, it could be established empirically that crystallites with diameters of less than 50 Å are present. The form of these aggregates is, however, at present still under debate; quantum wires^[2a] as well as so-called quantum dots and a quantum sponge have been proposed.^[4a] It is, however, clear that these samples have an extremely large inner surface of several hundred m² per cm³. This means that every tenth to hundredth(!) silicon atom is a surface atom. The inner surface is, after the preparation, initially passivated with hydrogen (SiH_x), which can be removed by thermal aftertreatment,^[2d] UV irradiation,^[6a] the use of electron beams,^[6b] or by air oxidation (formation of a SiO₂ surface as dielectric matrix).

A fundamental electronic property of this new silicon modification discovered by Lehmann and Gösele (Fig. 2) is the blue shift of the UV absorption edge by several hundred meV^[5, 6c] in comparison to that of c-Si. This effect is greater than that observed, for example, for amorphous silicon a-Si:H. The blue shift of the absorption edge^[6c, 9] can only be a result of quantum size effects on the energy states in the crystallite interior. By effective mass and tight binding calculations of the state density of porous silicon this effect can be confirmed quantitatively.^[7]

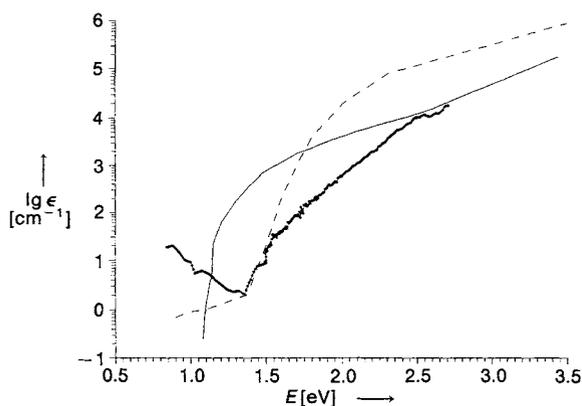


Fig. 2. The absorption edge of porous silicon (···) compared with that of c-Si (—) and that of a-Si:H (- -) according to [6c]. ϵ = absorption coefficient.

The most interesting electronic property of porous silicon is its photoluminescence. The mechanism of the photoluminescence is very complex, and separate experimental results appear at first to be contradictory. In the initial phase of the investigations this fact has led to the assumption of up to 13 hypotheses, which, however, can be based on three theoretical models. The first group includes models that ascribe the luminescence to recombination processes from quantum states in the interior of quantum wires^[2a] or quantum dots.^[2c] The second approach is completely different and is based on the assumption that luminescent molecules such as polysilanes^[8a] or siloxenes are found on the inner surface of porous silicon.^[8b] Besides these two extreme points of view, more recently several hypotheses were proposed and summarized to give a third model.^[6c] This consid-

ered, above all, discrete, energetically low-lying states on the crystallite surface (surface states) together with quantized states in the crystallite interior. As a result of new important experimental findings this third polycasual approach has become more and more likely.

The following experimental results speak against the second approach, namely that silicon-containing molecular compounds are present on the surface of porous silicon:

- An important counterargument is that the luminescence quantum yield of porous silicon and that of thermally oxidized (O₂) porous silicon (transformation of the hydrogenated SiH_x surface into an oxidized SiO₂ surface) are almost identical.^[9a] As is generally known, a surface film from SiO₂ shows, however, no red luminescence.^[9b] A convincing counterargument is also that nanocrystalline Si layers^[9c] deposited by CVD and thermally oxidized with O₂ as well as Si crystallites dispersed in ethylene glycol and oxidized show similar luminescence behavior.^[9d]
- On resonance excitation satellite bands are observed within the luminescence band, which confirm a moment-conserving phonon participation in the optical transitions.^[9e] These results are clearly in accord with the occurrence of recombination processes from energy states in the crystallite interior, but do not mean that siloxenes or polysilanes do not participate in luminescence processes.

Now let us consider the proof for energy states on the crystallite surface (model 3). Discrete surface states of lower energy can play an important role in recombination processes, and a series of experimental results can only be understood by the occurrence of such surface states:

- Raman spectroscopic studies on porous silicon show the Si-Si vibrational modes typical for small crystallites at 510–520 cm⁻¹. Furthermore, a broadened Si-Si vibrational band shifted to 480 cm⁻¹ is observed by IR spectroscopy (which is more sensitive to the surface), which can be explained by reconstruction of the Si-Si bonds on the crystallite surface. This surface reconstruction similarly leads to a broadening of the Si-H vibrational band in porous silicon in comparison with that of an ideal Si-H vibrational mode.^[9f]
- On the crystallite surfaces considerable quantities of “dangling bonds” (very stable Si radicals) can be detected by ESR,^[10a] ODMR (optical detection of magnetic resonance), and SDPC (spin-dependent photo-conduction) measurements.^[10b] This also agrees with a significant absorption below 1.11 eV in the spectrum of porous silicon, which can only be explained by the existence of deep crystal defects in the band gap. The concentration of Si radicals (dangling bonds), determined by ESR measurements, for samples with optimal luminescence is 10¹⁶ cm⁻³; a value which in turn is higher than that for amorphous a-Si:H. The spin density of porous silicon is increased up to 10¹⁹ cm⁻³ by degradation processes; the luminescence yield of these samples is inversely proportional to the spin density.
- Furthermore, the UV absorption edge of porous silicon changes significantly on saturation of the samples with H₂ (reaction of the radicals with the formation of Si-H bonds). The crystallite size remains unchanged. This is in agreement with the existence of discrete states on the crystallite surface, as discussed in reference [6c].

- Also “tight binding” calculations (which only consider the interactions with the nearest neighbors) confirm the occurrence of surface states (in the form of a reconstruction of the crystallite surface), which lie energetically lower than the quantum states of the crystallites.^[11]
- In addition, a red shift of the luminescence is observed on low-temperature oxidation (with constant crystallite size) or on aftertreatment of porous silicon, for example with propanol.^[12a]
- Finally, there is a great similarity between the time-resolved photoluminescent behavior of porous silicon and that of a-Si:H.^[9b] In amorphous silicon radiative recombination occurs—as proven—through so-called flat localized states (“Urbach tail”).

A more exact analysis of the time-, temperature-, and wavelength-dependence of the luminescence behavior of porous silicon shows that several mechanisms are active.

Apart from the above-mentioned luminescence band, porous silicon shows two further bands (Fig. 3). The band 2

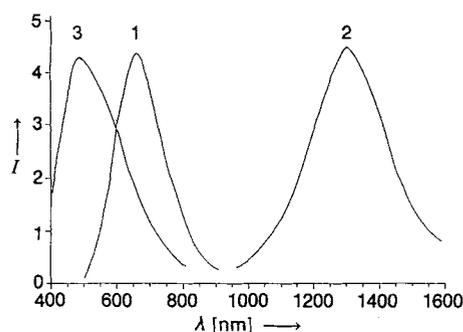


Fig. 3. Schematic representation of the three luminescence bands of porous silicon observed so far: 1: the red bands with slow decay times [2a,9e], 2: the IR band, which was first observed at 4.2 K [12b], and 3: the green-blue band [9e,12d] with rapid decay times.

lies in the region 0.8–1.2 eV^[12b,c] and was already observed in 1984 in photoluminescence investigations at 4.2 K, which in the meantime has been almost forgotten. Furthermore, by photoluminescence spectroscopy with different retardation times an additional luminescence band 3 at 2.3–2.5 eV was observed.^[12d,e] A special property of this band in the blue region is its extremely rapid decay time (10 ns or less in contrast to a few μ s for the luminescence of band 1). It could be shown that also the rapid decay of the luminescence of the band 3 is intrinsic for porous silicon.^[12e] Model approaches^[6c,13] provide preliminary explanations for the rapid luminescence (in the range of ns). However, for a better understanding of the three luminescence processes, especially of the latter two mentioned, still many investigations are necessary. All three observed luminescence channels can be of practical significance.

Silicon-containing molecular compounds—siloxenes and polysilanes: What are siloxenes? A siloxene is a layered polymer of $\text{Si}_6\text{H}_3(\text{OH})_3$. Characteristic for siloxene is probably the partial retention of Si–Si bonds in Si_6 rings, which are saturated by hydrogen substituents and linked together.

Siloxene is prepared by a topochemical hydrolysis reaction from CaSi_2 , which in all probability also has a layered

structure of Si_6 rings. Siloxene samples were described about 130 years ago by Wöhler,^[14a] and later by Hönigschmidt^[14b] and Kautsky.^[14c,d] The structural model with Si_6 rings, proposed by Kautsky and Hengge, was further refined by Weiss et al., who carried out X-ray structural investigations; however, the model has still not been completely proven since to date no suitable single crystals have been obtained.^[14e]

A detailed investigation of the photoluminescence properties of siloxenes is mainly the result of work by Hengge.^[14f,g] Renewed, intensive investigations and quantum mechanical calculations^[15] on siloxenes have been in progress for about two years. The most important experimental result obtained is the observation of a luminescence quantum yield in the percent range, which is comparable to that of porous silicon,^[16] and it is this behavior that has led to the renaissance of siloxene research.

Generally, the prepared siloxene samples are polycrystalline and undergo slow hydrolytic decomposition in the air. For siloxene samples that were annealed at temperatures of up to 400 °C, however, luminescence intensity (for shift of the peak position) remains almost unchanged.^[12a]

These results show that despite structural rearrangements the luminescence is retained. The cause of the luminescence of siloxenes as well as the structure of these compounds (do in fact only Si_6 rings occur or are there also larger silicon clusters present?) are by no means completely explained. The question must be posed whether the luminescence from siloxenes cannot also be ascribed to a nanostructure comparable to porous silicon.

Indeed, based on preliminary investigations by SAXS (small angle X-ray scattering), in siloxene structural domains of the size of 15–20 Å can be proven.^[17] These contradictory results certainly require further intensive research, including a possible examination of the structure of the radiative samples.

Furthermore, polysilanes are of interest as an additional class of molecular model compounds. For example, from the pioneering work by West on cyclohexasilanes, it is known that these form relatively stable radical anions and cations ($g = 2.0044$, dodecamethylcyclohexasilane, UV spectrum: $\lambda_{\text{max}} = 248$ nm, $\epsilon_0 = 5400$, $\lambda_{\text{max}} = 256$ nm (sh), $\epsilon_0 = 1100$), in which, according to results from ESR spectroscopy, the SOMO (semi-occupied molecular orbital) is delocalized over the whole Si_6 skeleton.^[18] According to investigations by Miller, Michl et al. polysilanes also show luminescence already at 293 K, albeit at 340 and 450 nm (excitation wavelength = 390 nm) with some astonishingly high quantum yields up to 70% and with a lifetime in the 0.1 ns range for the shortwave band. The mechanism of the luminescence of long-chain polysilanes has been studied in detail.^[19]

Considering the complex set of questions that still need to be answered, there is a significant overlap of molecular chemistry and solid-state physical problems, which can only be resolved by intensive cooperative work of chemists and physicists in this area.

Although the single models in future may require some modification, one thing is certain: Both porous silicon and nanocrystalline silicon in dielectric matrix, as well as silicon-containing molecular compounds such as siloxene and polysilane luminesce with similar quantum yields to GaAs!

The specific applications for which these materials are suitable will be shown by future developments.

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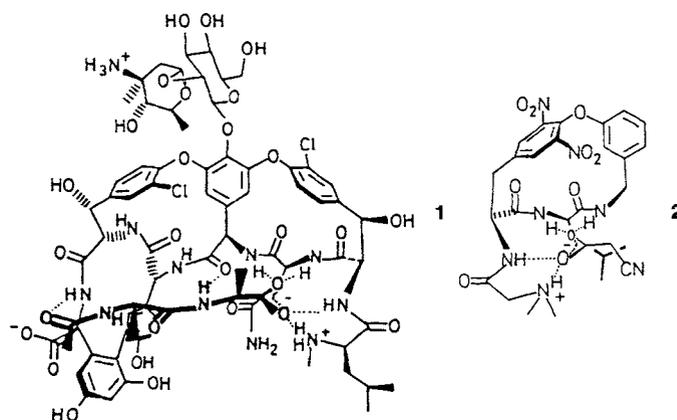
Models for Peptide Receptors

By Hans-Jörg Schneider*

The development of selective host compounds for reversible binding of peptides is one of the most interesting fields in biomimetic chemistry. The topic is of importance for the understanding of molecular recognition mechanisms including those in proteins, for analytical methods, which incorporate sensor technology, and for the preparation of stereochemically pure peptides. The efficient preparation of peptides with a completely or partially "nonnatural" configuration^[1] is a particularly attractive research area in medicinal chemistry because of the enormous diversity of biological activity of many oligopeptides. The therapeutically important stability of peptides against proteases, which often degrade the peptides, administered, for instance, as antibiotics, before they reach their target, can be significantly improved by the introduction of D-amino acids instead of L-amino acids.

In view of this importance and of the early success of the "chiral resolution machine" of Cram et al.,^[2] which uses crown ethers containing bisnaphthyl units to separate amino acids, it is somewhat surprising that the selective complexation of peptides by organic host compounds has not yet been

attempted on a very broad scale. The major noncovalent interactions for peptides have been analyzed by D. H. Williams et al. for the example of natural host vanomycin (**1**),^[3] which binds the carboxylate terminus of Ala-Ala sequences of a peptidoglycan precursor compound (highlighted in boldface superimposed on the structural formula of **1**). A model limited predominantly to the carboxylate binding niche of this antibiotic was obtained by Hamilton et al.^[4] in the form of compound **2**; the NMR spectrum of this model compound shows that a proton is transferred from bound



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