Porous Silicon: From Luminescence to LEDs

With its tunable light emission, room-temperature quantum efficiencies near 10% and increasingly efficient light-emitting diodes, porous silicon may hold the promise of fully integrated optoelectronic devices.

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Silicon is at the heart of the microelectronics revolution. Its dominance over other semiconductors is intimately tied to its superior materials and processing properties and to the tremendous base of technology that has developed around it. Another semiconductor is not likely to displace silicon as the material of choice in electronic applications. Silicon, however, is an extremely inefficient light emitter, and for this reason has not enjoyed the same level of dominance in optical applications.

The importance of developing a technology that would allow optical and electronic devices to be easily and inexpensively integrated on a silicon wafer has long been recognized. Such an advance would have a significant impact on display, communications, computer and a host of related technologies. In fact, a degree of optoelectronic integration on silicon wafers has been achieved. For example, high-quality optical detectors can be fabricated from silicon, and silicon charge-coupled device detector arrays are in common use. However, complete integration of optics and electronics requires putting light-emitting diodes (LEDs) and semiconductor lasers on the same wafer that contains detectors and electronic components. In today's technology, light-emitting semiconductor devices are fabricated almost exclusively from direct-bandgap compound semiconductors such as gallium arsenide and indium phosphide, which have much higher optical efficiency than silicon. Direct integration of compound semiconductor devices on a silicon wafer has proven to be very problematic.

An alternative solution to this problem is to improve the efficiency of silicon itself, or to develop an optically efficient silicon-compatible material. Considerable research has been directed at this approach using techniques that range from the engineering of superlattices and quantum wells composed of silicon, germanium and carbon to the doping of silicon with optically efficient rare earth atoms such as erbium. (See reference 1 for discussions of many of these approaches.) Researchers have made progress with many of these techniques, but room-temperature efficiencies sufficiently high to challenge compound semiconductor materials have until recently appeared to be out of reach.

In the fall of 1990, however, Leigh Canham of the UK's Defence Research Agency reported that one could obtain visible room-temperature photoluminescence from porous silicon layers formed on the surface of a silicon wafer.[2] The light-emitting properties that Canham reported for porous silicon were intriguing for several reasons. First, the emission energy was well above the bandgap of bulk silicon. Second, the energy (or color) could be tuned throughout the visible spectrum by changing the preparation conditions, an important consideration for display technologies that require red, green and blue devices. Finally, the quantum efficiency was comparable to that of direct-bandgap compound semiconductors.

Canham's paper generated worldwide speculation that a silicon-based optoelectronic technology was at hand, and it kicked off a flurry of research activity directed at porous silicon. Six years have passed since the initial report of room-temperature photoluminescence from porous silicon, and steady progress has been made in uncovering the fundamental properties of the mechanism of luminescence. Porous silicon's suitability for optoelectronic applications has also been an active area of research, and room-temperature LEDs with efficiencies greater than 0.1%—as well as test structures that integrate LEDs with electronic devices—have been fabricated (see figure 1). In this article, we summarize the status of the field and discuss issues that remain to be resolved if porous silicon is to provide the missing link between electronic and optoelectronic integration.

What is porous silicon?

Described simply, porous silicon is a network of nanometer-sized silicon regions surrounded by void space (figure 2). A porous silicon film is typically prepared by electrochemical anodization of the surface of a silicon wafer. Figure 2a is a schematic diagram of an electrochemical cell used to prepare porous silicon by anodic etching.

Although interest in the light-emitting properties of porous silicon is a rather recent development, porous silicon itself was discovered in 1956 during a study of methods for electropolishing silicon.[3] The relationship

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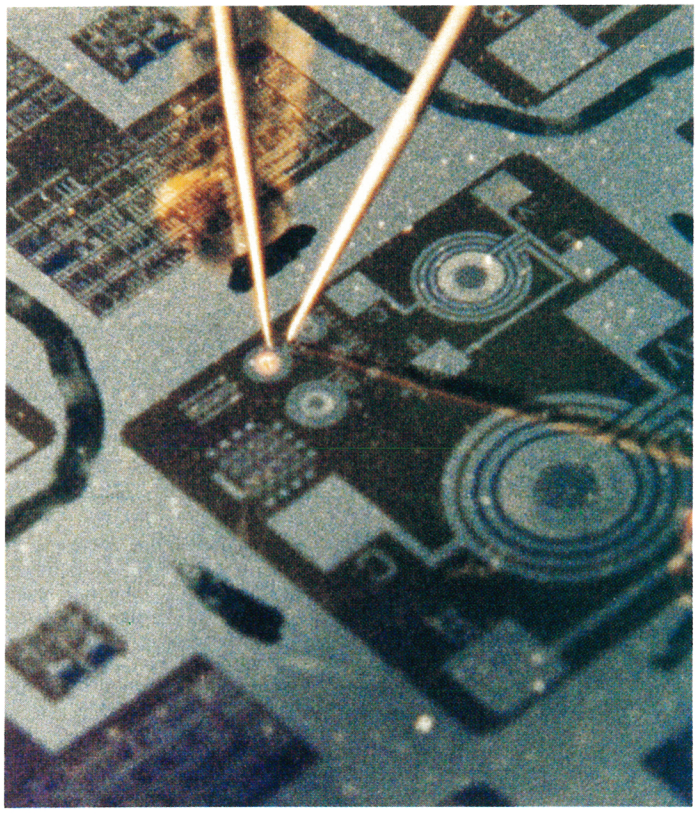

FIGURE 1. POROUS SILICON optoelectronic circuit in which a silicon bipolar transistor drives a porous silicon light-emitting diode integrated on the same wafer. Each set of concentric metal rings is a separate LED/transistor circuit. The rings are contacts to the transistor, which is circular in design and located under the rings. The LED is at the center of the rings. The small 0.3-mm-diameter disk of light at the convergence of the two contact wires is luminescence from the LED.

between fabrication conditions and the structural and electronic properties of porous silicon was examined extensively in subsequent work. The current density, hydrofluoric acid concentration, presence or absence of illumination during etching and, in particular, the doping type and resistivity of the silicon influence the morphology of the porous layer. For example, lightly doped p-type material tends to produce a spongelike pore morphology, whereas n-type material and heavily doped p-type silicon tend to give rise to dendritic or columnar features. Porosities (the fraction of void space) typically range from 50% to greater than 90%, with light emission generally occurring more efficiently for higher porosity.

Bulk silicon's low optical efficiency

To interpret the optical properties of porous silicon, it is important to understand why bulk silicon, which is an indirect-bandgap semiconductor, has a low optical efficiency. Figure 3 shows schematic band structures near the bandgap for a direct-bandgap semiconductor such as GaAs (figure 3a) and an indirect semiconductor such as silicon (figure 3b). These band structures give electron energies as a function of k, where $\hbar k$ is the "crystal momentum" of the electron. (Crystal momentum is the analog of classical momentum within a periodic lattice.)

Band-edge light emission from a semiconductor involves the excitation of an electron from the filled valence band to the empty conduction band and subsequent recombination of the electron with an empty state (or hole) back in the valence band. The de-excitation process is referred to as electron–hole recombination. Light emission occurs when the recombination energy is given off as a photon. In general, the recombination process must conserve both energy and crystal momentum. This requirement is analogous to the simultaneous conservation of energy and momentum in a classical two-body interaction.

In a direct semiconductor, the conduction-band minimum and valence-band maximum occur at the same value of k. Since the momentum of a photon is quite small, emission of a photon as a result of electron–hole recombination conserves k. Optical processes tend to be fairly strong in direct-gap semiconductors. In contrast, the conduction-band minimum and valence-band maximum of an indirect semiconductor occur at different points in k-space. Crystal momentum cannot be conserved through photon emission or absorption alone. Simultaneous emission of a photon and emission or absorption of another particle such a phonon (a lattice vibration) can conserve k, but such processes are second order, and therefore much less probable than direct optical recombination. For this reason, light emission from pure bulk silicon is found both to be much weaker than in direct-gap compound semiconductors and to involve the simultaneous emission of a photon and a k-conserving phonon. Typical room-temperature efficiencies for silicon are much less than 0.001%. In contrast, GaAs LEDs routinely have quantum efficiencies of 1–10%, and efficiencies approaching 30% are obtained for specialized LEDs.

Mechanism of luminescence in porous Si

The first report of luminescence from porous silicon at energies in excess of the silicon bandgap was made in 1984.[4] This study, however, was done at low temperature and did not report efficiencies. As mentioned above, strong interest in light emission from porous silicon really began with Canham's study in 1990, which demonstrated efficient, tunable, room-temperature light emission at energies well above the silicon bandgap. The tunability range is quite remarkable. As figure 4 shows, by varying the preparation conditions, the emission energy can be varied from the near infrared to the blue–green portion of the visible spectrum. At almost the same time that Canham's work appeared in print, Volker Lehmann and Ulrich Gosele, then at Duke University, published optical

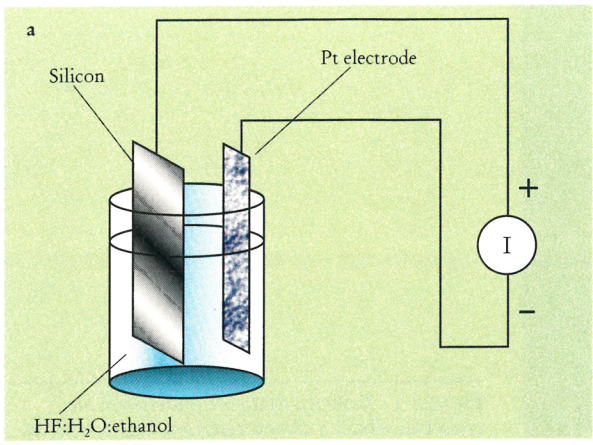

FIGURE 2. ANODIC ETCHING and result. **a:** Schematic diagram of an electrochemical cell used to prepare porous silicon. The cathode is made of platinum and the silicon acts as the anode. The electrolyte is a mixture of hydrofluoric acid, water and ethanol. The acid is the essential ingredient for etching (or dissolution) of the silicon, and the ethanol acts as a wetting agent. When a positive bias is applied to the silicon, a porous layer a few micrometers thick forms on the wafer. **b:** Transmission electron micrograph of porous silicon made from a p^+ silicon wafer. The sample was intentionally prepared to have a very open pore morphology. Pore sizes are on the order of 50 nm, and the interconnecting silicon network is made of columns with diameters of less than 10 nm. Silicon feature sizes in samples with the highest optical efficiencies are often closer to 2 nm, as discussed in the text. (Image courtesy of Anthony G. Cullis of the UK's Defence Research Agency.)

transmission spectra of porous silicon.[5] Their results also suggested that the bandgap of porous silicon was higher than that of crystalline silicon.

Much of the subsequent research on porous silicon has been directed at determining the mechanism of light emission. Not only is this a fundamentally interesting question, but it also has a direct bearing on the usefulness of the material in optoelectronic applications. In their initial reports, Canham and also Lehmann and Gosele suggested that the porous layers were made up of small, nanometer-sized crystalline silicon regions, and that the bandgap was being increased relative to bulk crystalline silicon as a result of quantum confinement in the nanocrystals. The applicability of this quantum confinement model to porous silicon has received considerable attention in the literature.

Figure 5a is a schematic of a semiconductor quantum well. Here, electrons in the conduction band and holes in the valence band are confined spatially by potential barriers—the surfaces of a nanocrystal, for example. As a result of the confinement of both the electrons and the holes, the lowest energy optical transition from the valence to the conduction band increases in energy, effectively increasing the bandgap. Within a simple effective-mass approximation, the confined gap is given by

$$E_{\text{confined gap}} = E_{\text{bulk gap}} + \frac{\hbar^2\pi^2}{2}\left[\frac{1}{w_x^2}+\frac{1}{w_y^2}+\frac{1}{w_z^2}\right]\left[\frac{1}{m_c^*}+\frac{1}{m_v^*}\right]$$

where m_c^* and m_v^* are the conduction and valence-band effective masses, respectively, and w_x, w_y and w_z are the dimensions of the confined region assumed to be a box. The size of the confined bandgap grows as the characteristic dimensions of the crystallite decrease. Quantum confinement is a well-known and carefully studied effect in such semiconductor systems as $GaAs/Al_{1-x}Ga_xAs$ heterostructures, in which it is frequently used to tune the energy of semiconductor lasers.

Figure 5b shows calculations, using this formula, of the optical bandgap of a silicon nanoparticle as a function of its characteristic dimension. We find a transition energy near 2 eV in the red part of the visible spectrum for a particle size of roughly 3 nm. In reality, this approach to calculating the transition energy is far too simplistic. It ignores the nonparabolicity of the conduction band, the detailed shape of the valence band and the influence of neighboring bands (given the large confinement energy), as well as excitonic contributions. Several groups have published the results of more sophisticated calculations.[6] Although the predicted bandgap is sensitive to the details of the models, the results, which tend to fall within the shaded region in figure 5b, show that the effective-mass model discussed above overestimates the bandgap for a given particle size. A 2 eV optical transition probably results from crystallites with a characteristic dimension nearer 2.0 to 2.5 nm.

A first step toward testing the quantum confinement model would be to determine if crystallites of this size make up a large fraction of the films. Assuming they do, then observing changes in the optical transition energy as the dimensions of the nanocrystals are changed would be fairly convincing proof of the model. Canham's original paper provided indirect evidence for this effect. He observed that the luminescence energy increased with longer etch time. If longer etch time leads to smaller nanocrystals, then we could conclude that size correlates with luminescence energy. Although this result is suggestive, it is possible that longer etching could also correlate with

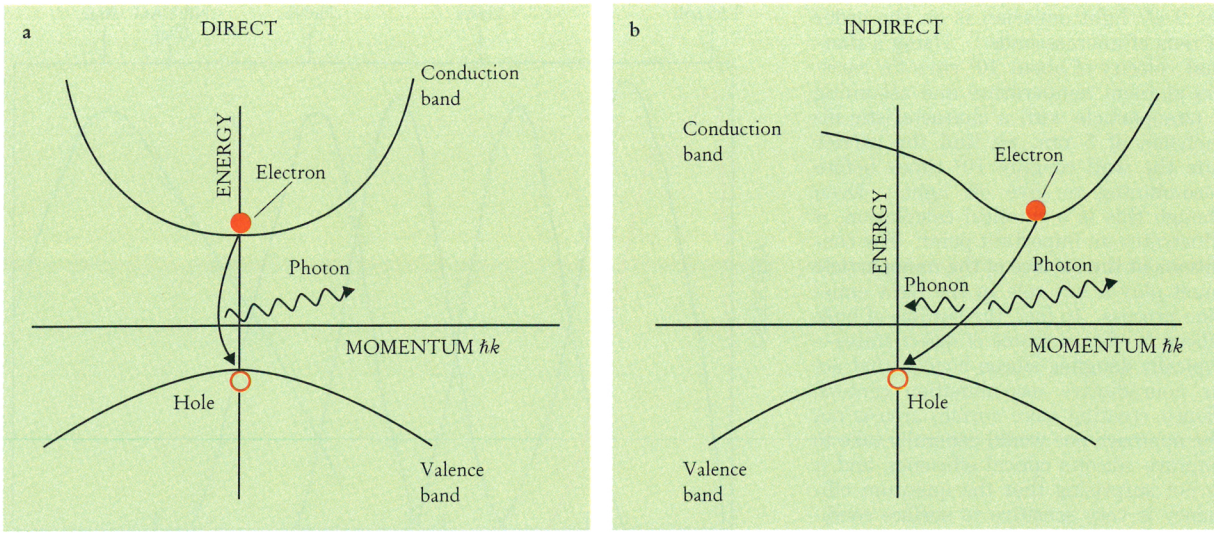

FIGURE 3. BAND STRUCTURE near the bandgap for a direct (**a**) and an indirect (**b**) semiconductor. In an optical transition, crystal momentum $\hbar k$ is conserved. **a:** Since photons carry very little momentum, direct optical transitions can occur only between conduction- and valence-band states that have the same value of k. In a direct semiconductor such as GaAs, the conduction-band minimum and valence-band maximum occur at the same value of k, and direct optical recombination of electrons and holes is relatively strong. **b:** In an indirect semiconductor, crystal momentum can be conserved only if an additional particle, such as a momentum-conserving phonon, is emitted (or absorbed) along with the photon. Because this is a second-order process, the optical efficiency for indirect materials such as silicon tends to be quite low relative to that of direct-bandgap semiconductors. The photon and phonon arrows are symbolic, not quantitative. In particular, the phonon carries most of the momentum but very little of the transition energy.

other changes in film properties, such as hydrogen or oxygen content or the density of surface defects. For this reason, researchers have sought more direct measurements of the correlation between feature size and energy gap. In fact, techniques such as transmission electron microscopy and Raman scattering have shown that crystallites with the proper dimensions are present in porous films.[1,7] Porous silicon, however, exhibits broad luminescence lines (figure 4), which imply correspondingly large particle-size distributions, and it has not been possible to use these methods to simultaneously measure the sizes of individual particles and their emission energies.

Testing quantum confinement

In spite of these difficulties, progress has been made in correlating feature size with energy. Some interesting results in this area have come from groups that have developed methods for chemically synthesizing freestanding silicon nanocrystals with dimensions of less than 10 nm.[8] The nanocrystals are found to exhibit efficient visible luminescence with properties quite similar to those of porous silicon. It seems likely that an explanation for the photoluminescence in nanocrystals will also apply to porous silicon films. As prepared, these nanocrystals have broad size distributions. William Wilson and his coworkers at what was then AT&T Bell Laboratories used liquid chromatography to separate the nanocrystals into different groups with larger or smaller average particle sizes. As figure 5c shows, the emission spectrum shifts to higher energy as the average particle size decreases. Stefan Schuppler and his colleagues at Bell Labs and Lawrence Berkeley National Laboratory used x-ray absorption studies to infer a crystallite dimension, which again decreases as the peak luminescence emission energy increases.

Another measurement that supports the quantum confinement view involves resonant excitation of the photoluminescence band. Figure 6a shows the luminescence spectrum from a porous silicon sample excited by ultraviolet light. Figure 6b gives a spectrum for the same sample obtained with an excitation energy in the middle of the luminescence band (resonant with the band). For the spectrum in 6b, the zero of energy is the position of the laser excitation line, and so the spectrum gives emission intensity as a function of the energy below the laser line. The positions of the steplike features in the spectrum correspond quite closely to the energies of the momentum-conserving phonons in crystalline silicon. This correlation strongly suggests that the luminescent species is crystalline silicon, even though the bandgap is far in excess of that of bulk silicon.

The presence of the phonons also suggests that direct optical recombination, which is expected to become allowed due to the loss of translational symmetry in the small crystals, is at most comparable in strength to indirect processes for emission near 2 eV. Primarily indirect recombination near 2 eV is consistent with theoretical arguments.[9] Phil Calcott and Keith Nash at the Defence Research Agency have shown that as the excitation energy increases, the phonon features broaden and become less distinct, which may indicate a growing direct transition contribution.[10]

To explain the luminescence from porous silicon requires more than accounting for the increased bandgap. We must also understand the material's surprisingly high optical efficiency in light of bulk silicon's low efficiency. Some interesting insights into this efficiency can be obtained from luminescence lifetime measurements. These measurements involve exciting electron–hole pairs with a pulse of laser light, and then monitoring the light emission as a function of time after the pulse to determine the rate at which the carriers recombine.

In general, the decay rate in porous silicon is found to depend on the luminescence energy, but for the present discussion we wish only to note that a typical decay time

for 2 eV light emission is on the order of tens of microseconds.[11] Using a thermal velocity of about 10^7 cm/s for carriers at room temperature and assuming a nanoparticle with a characteristic dimension of 5 nm, we find the carrier hits the wall roughly 10^9 times before recombining to give off light. Even though this is a classical calculation, it illustrates an important point. The conditions at the surface of the nanoparticle must play a key role in the light emission process. In fact, the surface of bulk silicon is often a source of defect states—typically dangling silicon bonds—that act as nonradiative recombination centers. Hence, creating more surface area is not the approach one would generally take to improve silicon's optical efficiency, and it is not surprising that the quantum efficiency is very sensitive to surface condition and treatment.

Freshly prepared porous silicon contains a high density of hydrogen, as seen, for example, in infrared transmission studies and in x-ray absorption measurements.[12,13] Hydrogen terminates dangling bonds at the silicon surface. In spite of porous silicon's extremely high surface area, the density of dangling bonds in freshly prepared material can be below the detectability limit of electron paramagnetic resonance. The freshly prepared surface appears to be well passivated, and its optical efficiency is quite high—reports range from 1 to 10% external quantum efficiency at room temperature. Hydrogen-terminated material, however, shows substantial susceptibility to room-temperature oxidation and hydrogen loss, both of which lead to reduced optical efficiency.[12] Although the sensitivity to surface condition is generally undesirable for device applications, reversible changes in the luminescence emission spectrum caused by adsorption and removal of chemical species from the porous surface have been observed. Michael Sailor's group at the University of California, San Diego, has suggested that this effect might be useful in making chemical detectors.[7]

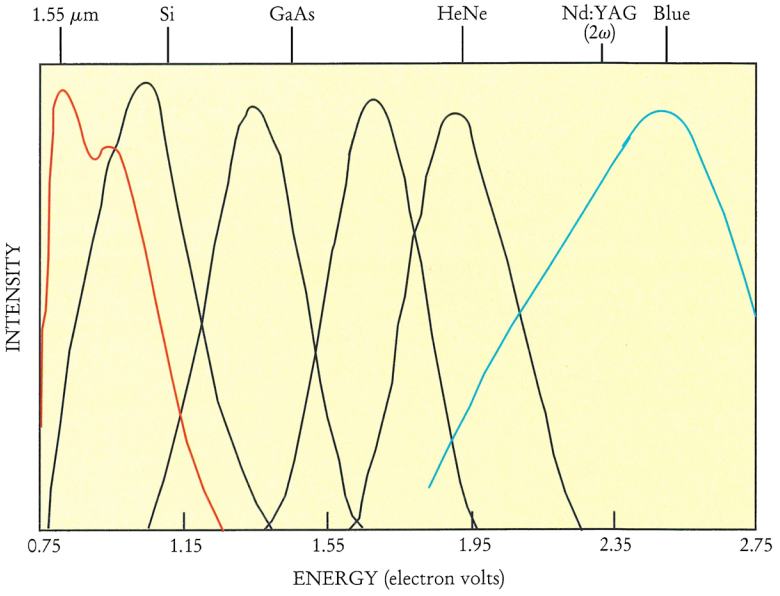

FIGURE 4. PHOTOLUMINESCENCE SPECTRA from a sequence of porous silicon samples at room temperature. The spectra are normalized. Different emission energies were produced by varying the preparation conditions. Infrared emission at energies less than the silicon bandgap, such as observed in the lowest energy curve in this figure, is probably defect related. High-energy blue luminescence, which is observed in heavily oxidized samples, has been attributed to the oxide rather than the silicon; the highest energy spectrum in this sequence was obtained from an oxidized sample. These two emission bands should be distinguished from the efficient tunable luminescence represented by the remaining curves in the figure. It is this intermediate emission band that is the subject of this article. By varying the preparation conditions, the energy of the band can be tuned from the near infrared into the blue/green part of the visible spectrum with room-temperature efficiencies near 10%. For comparison purposes, characteristic energies of common light sources (HeNe laser and frequency-doubled Nd:YAG laser), semiconductor bandgaps (Si and GaAs) and fiberoptic links (1.55 μm) are indicated at the top of the figure.

The need for a more stable surface termination has naturally led to studies of SiO_2 as a surface passivant. As mentioned above, low-temperature thermal oxidation of porous silicon results in poor optical efficiency. In contrast, several groups have reported the successful preparation of efficiently luminescing material by anodic oxidation or rapid thermal oxidation of porous silicon. These processes result in higher quality oxides that leave a surface with few nonradiative defects to degrade the efficiency. As expected, porous silicon terminated by high-quality oxide shows improved luminescence stability.

Other possible mechanisms

Although the quantum confinement model has received the most attention in attempts to understand light emission from porous silicon, other explanations have also been advanced. The large surface area of porous silicon, and the sensitivity of its optical efficiency to surface conditions, have caused some to speculate that light emission may arise from a molecular species, defect or alloy produced when the silicon is anodized. For example, the large hydrogen concentration in freshly prepared material has led to the suggestion that a silicon–hydrogen alloy effect is responsible for the luminescence. Another interesting explanation that has generated considerable discussion attributes the optical properties to siloxene ($Si_6O_3H_6$), a silicon-based compound that is purportedly produced on the silicon surface during anodization (see the articles by Martin Brandt and his coworkers in the books in reference 7). SiO_2-related defect centers are another suggested source of the luminescence. The absence of appreciable amounts of oxygen in freshly prepared porous silicon, or of hydrogen in rapidly thermally oxidized porous silicon, is inconsistent with these explanations, assuming we wish to find one model to account for the luminescence in all forms of porous silicon. Although it is certainly possible that minority amounts of some of these species may exist in porous silicon and even contribute to the luminescence, it is unlikely that the majority of the luminescence can be attributed to their presence. As a result, these models have largely been abandoned.

Finally, we note that in our explanation of the quantum confinement model given above, we tacitly assumed that the optical bandgap and the luminescence emission energy were very nearly the same. If light emission occurs from defect states, this may not be a valid assumption. Fredrick Koch of the Technical University of Munich has

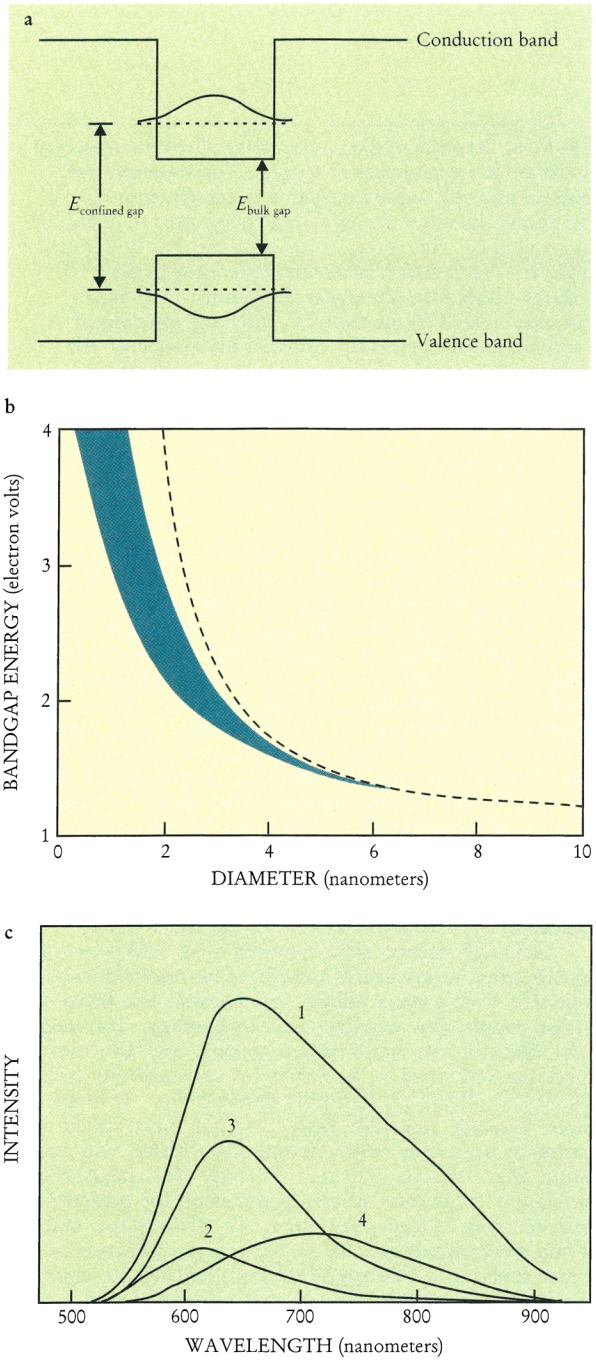

FIGURE 5. QUANTUM CONFINEMENT. **a:** Schematic diagram of a one-dimensional semiconductor quantum well. The ground-state conduction-band and valence-band wavefunctions and energy levels are shown. $E_{bulk\ gap}$ is the bandgap of the bulk, unconfined semiconductor. $E_{confined\ gap}$ is the lowest energy optical transition from the valence band to the conduction band of the quantum well. Confinement effectively increases the bandgap of the material. **b:** The dashed line is the bandgap of a silicon nanocrystal calculated as a function of crystal size using the effective-mass approximation given in the text. Three-dimensional confinement in a cubic box has been assumed. The bandgaps predicted by more sophisticated calculations exhibit model-dependent variations. The results of such calculations generally fall within the shaded region indicated in the figure. In spite of the variations, all of these models tend to give a smaller bandgap for a given particle size than does the effective-mass approach. **c:** The photoluminescence from a distribution of silicon nanocrystals is shown in spectrum 1. Spectra 2–4 were obtained after separating the nanocrystals by size using liquid chromatography. There is a clear correlation between the average crystal size, which decreases in going from 4 to 3 to 2, and the corresponding luminescence band energy. (From ref. 8.)

proposed a model in which absorption occurs into the quantized states of silicon nanoparticles in agreement with the pure quantum confinement model, but after absorption the carriers relax into surface-related defect states with light emission occurring when carriers in the defect states recombine (see the article by Koch in reference 1). One way to distinguish between the pure quantum confinement model and the extended model proposed by Koch is to look for a shift between the true bandgap of the porous silicon and the emission or luminescence energy. Evidence for such shifts has been reported from studies of optical absorption, photoelectron spectroscopy and more recently the redox potentials of porous silicon. (See reference 14 for a discussion of these results.) At the same time, other experiments seem inconsistent with a large difference between the absorption threshold and the emission energy. For example, the energies of the crystal momentum-conserving phonon thresholds in figure 6 should also show this shift, but none is observed.

Although there is mounting evidence that quantum confinement plays an essential role in the mechanism of luminescence from porous silicon, a definitive experiment that can distinguish, for example, between the pure quantum confinement model or the extended model proposed by Koch remains to be performed. It seems likely that clarifying the role of quantum confinement and, ultimately, the mechanism of light emission will require advances either in the preparation of samples with more uniform size distributions, or in techniques that allow one to investigate single nanoparticles. Some progress has already been made in both areas. The work on freestanding silicon nanoparticles discussed above goes a step in the direction of obtaining more uniform nanocrystals. Other intriguing approaches are being explored, such as the production of clusters of silicon atoms by laser vaporization followed by size selection of the clusters by mass spectroscopy.[15] From the characterization side, scanning probe microscopies such as scanning tunnelling microscopy have been applied to porous silicon and may be a productive area to investigate as a way of correlating photoluminescence signals with feature size.

Prospects for electroluminescent devices

Porous silicon's high luminescence efficiency under optical excitation is quite remarkable, but if the material is to have practical applications as a light emitter, it will be necessary to obtain similar results during electrical injection of carriers. Not surprisingly, attempts to observe electroluminescence began as soon as the high photoluminescence efficiency of porous silicon became public. Initial results on devices with solid-state contacts were not very encouraging. Liquid contacts, however, proved the existence of efficiencies that could be useful in real devices. Very early in the study of light emission from porous

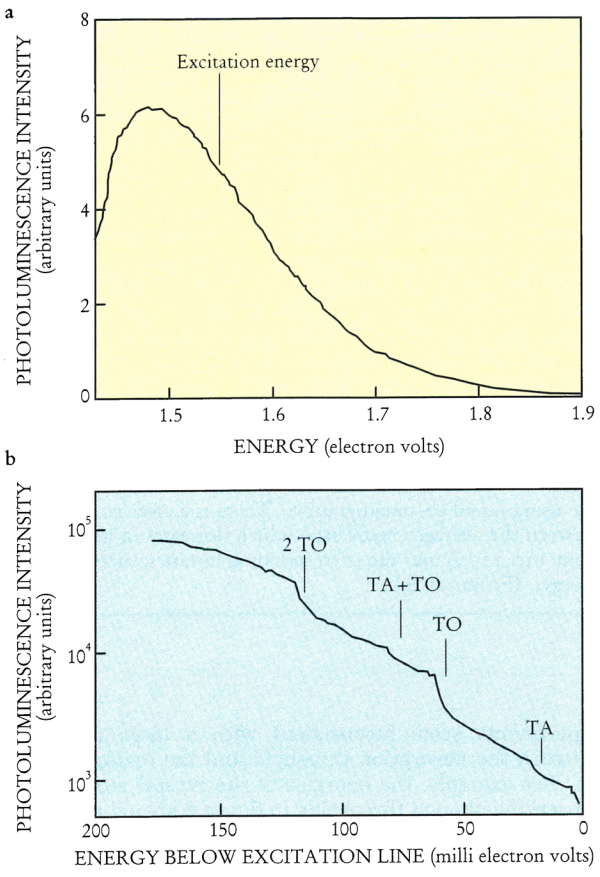

FIGURE 6. RESONANT EXCITATION. **a:** Photoluminescence spectrum for a porous silicon sample. The spectrum was obtained using ultraviolet excitation at energies near 3.0 eV. The pointer indicates the excitation energy used to obtain the spectrum in **b**. This energy is resonant with the luminescence band. **b:** The resonant photoluminescence spectrum. Features arising from the transverse acoustic (TA) and tranverse optic (TO) momentum-conserving phonons of crystalline silicon are clearly visible in the spectrum. All measurements were made at liquid-helium temperatures.

silicon, electroluminescence was observed during anodic oxidation in aqueous solutions of KNO_3 or HCL. (See the articles by Sophie Billat and her coworkers in the books in reference 7.) This luminescence, while very bright, lasted only a few minutes. Somewhat more stable light emission with liquid contacts was subsequently reported in aqueous electrolytes containing persulphate ions and in formic acid solutions.[16] External quantum efficiencies obtained in these electrolytes were in the neighborhood of 0.1%.

The first solid-state light-emitting devices were simple LEDs (often fabricated by evaporating a thin metallic electrode onto a porous layer), and their characteristics were far from ideal. Light emission typically required the application of relatively high voltages; emission was often observed with equal intensity in forward and reverse bias; and quantum efficiencies were less than 0.001%. It is not surprising that difficulties should arise in making efficient solid-state LEDs from porous silicon. In a photoluminescence experiment, absorption of a photon creates an electron and hole in close proximity to one another, probably within a single nanocrystal, where they can easily recombine. In an LED, light emission requires the transport of electrons and holes from opposite sides of the diode into the depletion region, where they recombine. This means that carriers must follow a tortuous path through the porous network. The nature of transport through this network is poorly understood. Even if transport through the network is possible, contacts that allow electrical injection of carriers into the porous layer and that do not short it out must be fabricated. Liquid contacts have an obvious advantage over solid-state contacts in terms of making an intimate electrical connection to the entire porous network.

The past year has seen substantial progress in dealing with these issues, and external quantum efficiencies of 0.1% or slightly better are now being reported for solid-state devices.[17] In these structures, implants are used to define a *pn* junction in a silicon wafer. Electrochemical anodization is then used to form a light-emitting porous layer that is embedded in the depletion region of the junction. Device characteristics, although still not ideal, have improved noticeably. For example, electroluminescence is observed only in forward bias and at voltages as low as 2 V. Maximum efficiency is obtained for operating voltages of approximately 5 V. This brings the required voltages for light emission into a range that is compatible with silicon electronics as demonstrated in figure 1, which shows a porous silicon LED being driven by a silicon transistor that was fabricated on the same wafer.[18]

Although recent achievements with LEDs are quite encouraging, many issues remain to be resolved before we conclude that porous silicon can become the basis for a silicon-compatible optoelectronic technology. The long optical lifetime can limit device speeds, and the emission spectrum will need to be narrowed substantially to avoid dispersion effects in fiberoptic applications. It is also not clear whether injection lasers, which have much more stringent materials requirements than LEDs, will ever be made from porous silicon. Perhaps the most serious constraint on porous silicon is the need for compatibility with existing silicon processing. In this regard, stability of the electroluminescence in particular continues to be a major concern. LEDs prepared from hydrogen-terminated porous silicon exhibit degradation similar to that seen in photoluminescence from hydrogen-terminated material (as discussed above). Stability is much better when an annealing step is added to create a thin oxide passivation layer on the porous surface, but because SiO_2 is an insulator, careful control of oxide thickness is critical to device performance.

Future

The six years that have passed since the discovery of efficient, visible, room-temperature photoluminescence from porous silicon have seen a steady advance in our understanding of the mechanism of luminescence. In addition, recent progress in realizing electroluminescence efficiencies comparable to the photoluminescence efficiency is promising. Still, fundamental issues remain to be resolved before the essential question, and the driving force behind the work on porous silicon, can be addressed:

Will porous silicon finally enable optical and electronic technologies to be integrated on a single silicon chip? The potential payoff, should the answer be yes, ensures that the materials science, electronic and optical properties of silicon nanostructures will remain active and exciting research topics.

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