

SiH_x excitation: An alternate mechanism for porous Si photoluminescence

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We show that low-temperature (230–390 °C) desorption of hydrogen from 0.1 Ω cm *p*-type porous Si structures leads to a redshift and gradual disappearance of the photoluminescence (PL). Furthermore, no blueshifting of the PL peaks is apparent with pore-widening treatments. These results are consistent with a luminescence mechanism from hydride species formed during the etching process. Based on this model, the PL intensity is expected to be most affected by total surface area of the porous silicon and the PL peak position by the hydride complex distribution.

Highly porous silicon layers fabricated by electrochemical etching have recently been the subject of great interest due to their room-temperature visible (600–800 nm) light-emission properties.^{1–3} Porous silicon was produced by electrochemical etching to generate a porous structure,⁴ followed by a pore-widening treatment to decrease the dimension of the pore walls.¹ This procedure results in highly porous Si, with porosities approaching 80%. It has been suggested^{1,3} that the remaining Si was in the form of thin quantum wires, with cross-sectional dimensions on the nanometer scale. It was also suggested that the dimensions were small enough to produce quantum size effects in the Si band structure.^{1–3}

The case for quantum confinement is based on several factors. First, the photoluminescence (PL) peak was observed at room temperature and its peak position was in the range of 600–800 nm,^{1,2} significantly blueshifted from the bulk Si band edge at 1.1 μm. Similar results were obtained in the case of the absorption edge by Lehmann and Gosele.³ Furthermore, the pore widening procedure resulted in a blueshifting of the PL peak with increasing etch time.² Because in the quantum confinement case blueshifts of the band gap are expected as the confinement size is reduced, these experimental results have been used as evidence that quantum confinement was the source of the visible photoluminescence from porous Si.

In this paper, we report an investigation of the mechanism of light emission in porous Si structures. We present results which show that, unlike previous works, we are able to form luminescing silicon in which the PL does not blueshift with pore widening. In addition, by studying the PL *in situ* under high vacuum conditions, we show that the visible PL in these samples disappears when hydrogen is desorbed from the porous structure. The evolution of hydrogen begins to occur at 230 °C, which is far below temperatures which would be expected to cause structural changes in silicon. Based on our observations, we will suggest a model for the light emission in which the visible PL is explained by the presence of SiH_x complexes, rather than quantum confinement.

The substrates used were boron-doped 1.0 and 0.1 Ω cm

p-type and 0.1 Ω cm *n*-type silicon (100) wafers. Porous 12-μm-thick silicon (0.1 Ω cm) layers of ~42% porosity were formed by etching the Si in a 25% hydrofluoric (HF) solution at a current density of 10 mA/cm². The porosity was increased by subsequent chemical etching in 25% HF solution for 0, 2, or 4 h.

In the vacuum experiments, the samples were introduced into an ultrahigh-vacuum chamber (base pressure ~3 × 10⁻¹⁰ torr) equipped with a Dycor quadrupole gas analyzer and optical access to allow the monitoring of *in situ* PL as a function of heating. The sample was heated resistively and its temperature was monitored using an Ircon 300C pyrometer, assuming an emissivity of 0.46.

The 488-nm line of the Ar⁺ laser was used for excitation and the PL was detected using a series of lenses, a ¼-m single grating monochromator with a 600 grooves/mm grating, and a silicon *p-i-n* detector. All of the PL data were normalized to the grating response which was measured using a tungsten lamp.

Infrared (IR) transmission measurements were also performed on porous silicon samples formed under the same etching conditions as those studied in the vacuum chamber. The data were recorded (versus air as a reference) at 4-cm⁻¹ resolution using a Fourier-transform system. Data are plotted as absorbance [= -log₁₀(*T*), where *T* is the transmittance]. Annealing of these samples was performed under an argon ambient and under high vacuum (~1 × 10⁻⁸ torr). Finally, the overall structure of the annealed porous silicon was examined using scanning electron microscopy (SEM).

We begin with the PL spectra of as-prepared, unannealed samples. Shown in Fig. 1 are three PL spectra of porous Si taken after 0, 2, and 4 h of pore widening in 25% HF. The samples used in this series were boron-doped *p*-type Si with a bulk resistivity of 0.10 Ω cm etched at a current density of 10 mA/cm². The most important observation is the lack of any significant blueshift in the PL peak with increasing pore widening times. The only major differences in the data are in the peak intensity, which is largest at 2 h. These data are inconsistent with quantum confinement, and differ from earlier results on

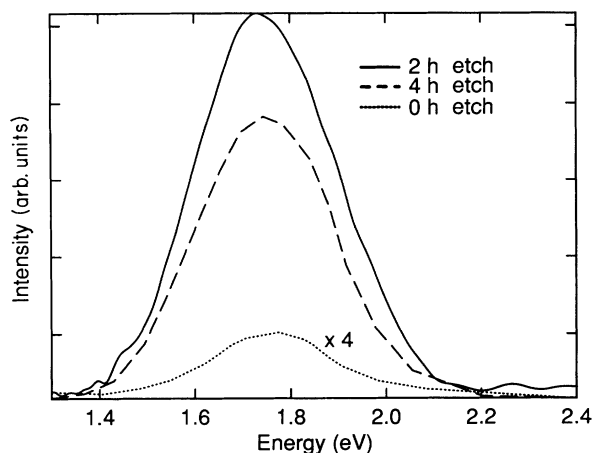


FIG. 1. PL spectra for 0.1 Ω cm *p*-type porous silicon samples etched electrochemically (10 mA/cm²), followed by a pore widening treatment in 25% HF for 0, 2, and 4 h.

10 Ω cm *p*-type Si.²

We have also used temperature-controlled desorption and mass spectrometry to investigate the role of hydrogen in the porous Si structures. Three separate samples were annealed in vacuum at temperatures ranging from 200 to 1200 °C for 1 min intervals. Figure 2(a) shows a series of PL spectra for one of these samples as a function of annealing between 230 and 390 °C. The unannealed (20 °C) sample in Fig. 2(a) has a PL spectrum similar to those reported in the literature. It is clearly evident in Fig. 2(a) that the PL intensity decreases very noticeably at temperatures as low as 250 °C, and almost totally disappears at 390 °C. In addition, the PL peak position shifts toward lower energy as the annealing temperature increases, resulting in a 0.15-eV shift in the temperature range shown in Fig. 2(a). Similar results were obtained

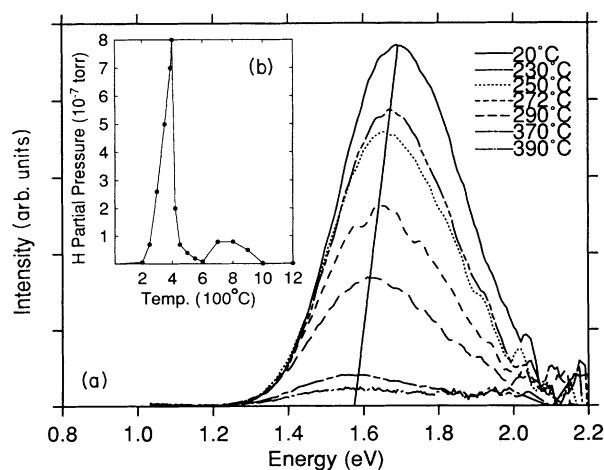


FIG. 2. (a) Decay in PL for UHV annealed 0.1 Ω cm *p*-type porous silicon in the temperature range of 20–390 °C and (b) the hydrogen gas evolution for the same sample as a function of heating.

for both *p*- and *n*-type samples.

The gas desorption from the sample during annealing was monitored as a function of temperature and time using the mass spectrometer. The results indicate that, in addition to a small amount of water and CO desorption, a very large desorption of hydrogen occurred. This is evident in Fig. 2(b), in which the hydrogen partial pressure is plotted versus the annealing temperature. Clearly, the greatest amount of hydrogen desorbs in the same temperature range as that in which the disappearance of intensity and shift of energy of the PL is observed.

Figure 3 shows IR transmission data in the Si-H bond-stretching region for the porous Si as a function of annealing in high vacuum ($\sim 1 \times 10^{-8}$ torr). The data support the thermal desorption results by verifying the loss of hydrogen from the sample over the same temperature range as the strong mass spectrometer signal was detected. The peaks in the 2080–2140 cm^{-1} range correspond in energy to those reported^{5,6} for monohydride, dihydride, and trihydride functional groups on Si surfaces. These spectra do not differ sufficiently from those reported by John *et al.*⁷ for polysilane chains or from spectra for H on Si surfaces^{5,6} to allow us to comment on the presence or absence of such chains in the present samples. Spectra in the 600–950 cm^{-1} range (not shown) exhibit SiH_x bending and deformation modes^{5,6} which correlate with the stretching modes in Fig. 3, and they too disappear after a 450 °C anneal. The origin of the weak band at about 2100 cm^{-1} remaining after the 450 °C anneal is uncertain. It may be due to H which has diffused into the bulk during the electrochemical etching process, since hydrogenated microcrystalline Si shows⁸ a band at 2100 cm^{-1} which survives annealing at 400 °C. This H may also be responsible for the desorption band between 600 and 1000 °C, in Fig. 2(b).

The peaks in Fig. 3 near 2195 and 2260 cm^{-1} are too high in energy to be assigned to pure hydride species and are, instead, attributed to Si-H stretching modes in which the Si is backbonded to one or more oxygen atoms.^{9,10}

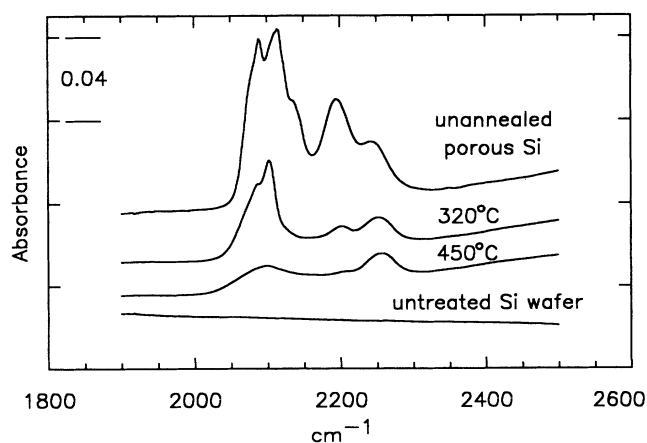


FIG. 3. Transmission spectra of *p*-type 0.1 Ω cm porous Si. Spectra are shown for a Si wafer, for unannealed porous Si, and after two anneals in vacuum.

This is supported by IR data for samples annealed in an Ar atmosphere rather than in vacuum. Here trace H₂O and/or O₂ impurities in Ar lead to oxygen adsorption (as shown by gradual development of an SiO₂-like spectrum in the 400–1400 cm⁻¹ range) and significantly more intense 2195 and 2260 cm⁻¹ bands in spectra recorded after annealing.

The SiH_x peaks and the PL intensity could be easily regained by dipping in a HF solution for a second. In addition, electron-spin-resonance experiments that were performed on unannealed, annealed and HF dipped samples¹¹ show a relatively small change in dangling-bond densities (from 2×10¹⁶/cm³ to 7×10¹⁶/cm³) in the temperature range where most of the PL disappears (450 °C or so). This seems to suggest that the PL quenching cannot be solely due to surface dangling bonds.

Structural studies of unannealed and annealed porous Si samples were performed by SEM. The 0.1 Ω cm *p*-type porous Si structures appeared as a pore network similar to a sponge; no silicon “wires” were evident.¹ No noticeable structural changes occurred for 1 min anneals at low temperatures (<400 °C) where the PL rapidly decreased in intensity, but changes began to occur at higher temperatures (>800 °C). At high anneal temperatures (*T* > 1000 °C), where all oxygen related complexes desorb and at which point silicon surface diffusion is significant, the structures formed Si balls, 500–2000 Å in diameter, and no pore network remained.

The above series of experiments shows two main results: First, the blueshift of the PL as a function of pore widening is not a universal phenomenon, and second, the loss of hydrogen from the porous structures is correlated with the disappearance and shift in energy of the PL. In order to examine how these results can help in the determination of the luminescence mechanism, it is useful to discuss briefly the behavior observed in amorphous hydrogenated Si (Refs. 12 and 13) and hydride complexes.¹⁴

Wolford *et al.*¹³ have reported room-temperature PL resulting from hydrogenated amorphous silicon (*a*-Si:H) deposited by homogeneous chemical-vapor deposition at low temperatures. Their results indicate a 5 K luminescence in the range of 1.3–2.05 eV, blueshifting with increasing hydrogen content. Those samples with the highest H content (PL at 1.8–2.0 eV) exhibited room-temperature luminescence. The presence of hydrogen complexes [SiH, SiH₂, SiH₃, or (SiH₂)_{*n*}] was used to explain this luminescence. The polysilane chains (SiH₂)_{*n*} result in a material with a larger band gap than in Si.¹⁴ In addition, even the monohydrides can lead to band-gap enlargements based on tight-binding descriptions of Si-H bonding. These models¹⁵ show that the presence of monohydrides leads to bonding states that are formed deep within the silicon valence bands. With higher H content, such as SiH₂ structures, even deeper states occur, expanding the gap even more. These calculations¹⁵ have shown that a large gap increase occurs as a function of increasing hydrogen content in the complex, and for 30% hydrogen, the band gap increases to 1.7 eV. This result has also been confirmed experimentally,¹⁶ where a 500 °C anneal of *a*-Si:H resulted in a significant hydrogen loss, and in a band-gap reduction of 0.2 eV.

Previous work suggested¹⁷ that the porous silicon surface is hydrogen terminated; our results indicate this and show the presence of hydride complexes. Furthermore, the IR signal from the SiH_x groups of the porous silicon is similar to the signal seen by Scott *et al.*¹⁸ in the *a*-Si:H material studied by Wolford *et al.*

We now propose a model that is consistent with all available data and does not require the existence of quantum confinement. It is known that porous silicon consists of small interconnected pores,¹⁹ which will clearly have very large surface to volume ratios. Thus, a significant number of the SiH_x structures can be present. It has already been shown by Wolford *et al.*¹³ that these hydrides can exhibit room-temperature luminescence in the range of interest, and so it seems reasonable to extend this idea to porous silicon. The disappearance of the PL with hydrogen desorption can thus be explained by the disappearance of these hydrides at higher temperatures, as shown by our IR results. Furthermore, the 0.15-eV redshift seen as a function of hydrogen desorption is then easily understood, since it has been established that shrinking of the band gap occurs with decreasing hydrogen content.^{15,16}

The behavior of the PL for the 0.1 Ω cm *p*-type porous silicon as a function of chemical etching (Fig. 1) can also be easily explained in terms of this model. If one considers that the PL intensity is a function of total number of the SiH_x complexes present in the porous silicon, then at low porosities (small Si surface areas), the intensity is low. Initially as the porosity increases, the surface area increases (number of SiH_x also increases), and so does the PL intensity. At some point, the etch begins to dissolve the walls of the porous structure, leading to a decrease in total surface area and a drop in the PL intensity. Note that no PL peak shift should be observed, since the chemical process results in a surface saturated with SiH_x, and in equilibrium, *x* should not be changing; only the number of these complexes changes. By contrast, in the desorption experiment, the average value of *x* changes as well as the total concentration of SiH_x complexes, resulting in both a shift and an intensity change in the PL. This result, however, is difficult to explain by sole recourse to quantum confinement effects.

As already mentioned, previous results² indicated a PL blueshift with pore widening for 10 Ω cm *p*-type silicon. We observed similar blueshifts in the case of lower-resistivity silicon (1 Ω cm). In those samples, however, the presence of a surface microstructure appears responsible for the shifts in the PL. These results will be published elsewhere.²⁰

In conclusion, we have shown that no shifting with energy of the PL has been seen in the pore widening process of 0.1 Ω cm *p*-type silicon samples. Furthermore, we have also established that the PL from *p*-type porous silicon redshifts and disappears as a function of hydrogen loss, and it can be recovered by dipping in HF. In addition, the small change in the dangling-bond density for unannealed samples and those which have lost most of the PL intensity further suggests that the loss of the PL cannot be solely explained by nonradiative quenching of the luminescence, but may be related to the fact that luminescing SiH_x complexes are lost after the anneals. Since the combination of

these results is quite difficult to explain solely by quantum confinement theory, we have suggested an alternate mechanism which can explain not only the data, but is consistent with other published results. This mechanism involves the luminescence from hydride complexes-poly-silanes, and the PL is most strongly affected by the total surface area and the hydrogen fraction of the hydride

complex. The former leads to PL intensity changes, while the latter to PL peak position shifts.

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