

## Light emission from porous silicon

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**Abstract.** Room-temperature visible luminescence observed in porous silicon is one of the most significant discoveries of this decade as it opens up the possibility of silicon-based optoelectronics afresh. The exact mechanism of this different luminescence behaviour of porous silicon, compared to crystalline silicon, is not well established. In this paper results of a combination of infrared absorption, and photoluminescence emission and excitation spectroscopies will be described to show that the nanocrystallite nature of porous silicon and chemical environment at the surface are the important aspects of this novel luminescence behaviour.

**Keywords.** Porous silicon; luminescence; optoelectronic materials.

### 1. Introduction

The selective electrochemical dissolution of crystalline silicon in hydrofluoric acid (HF) results in an interconnected network of nanocrystallites of silicon known as porous silicon (PS). After its discovery during early silicon technology research at Bell Laboratories (Uhlir 1956), it was used as an insulator in silicon on insulator (SOI) technology presently known as fully isolated porous oxidized silicon (FIPOS) (Bomchil *et al* 1989). The electrochemistry of formation of PS has been extensively studied during the development of this technology and has recently been reviewed (Smith and Collins 1992; Bomchil *et al* 1993). Although the optical properties of this material have been studied earlier (Pickering *et al* 1984), the novel visible luminescence at room temperature was reported only recently (Canham 1990). This material shows good promise for silicon-based light emitters (Koshida and Koyama 1992; Namavar *et al* 1992; Steiner *et al* 1993) and also for better photodetection (Yu and Wie 1992; Zheng *et al* 1992a).

The understanding of the mechanism of this novel luminescence behaviour is reasonably good, but not complete. The visible luminescence observed in PS at significantly higher energies than the band gap of crystalline silicon had been originally explained in terms of direct radiative recombination of electrons and holes in quantum-confined silicon wires (Canham 1990; Lehmann and Gösele 1991) which form the basic network of PS layer. The blue shift observed in the emission energy by reducing the width of the silicon wires further supported this hypothesis (Bsiesy *et al* 1991). The anomalous temperature dependence of photoluminescence (PL) emission energy and intensity indicate that the observed PL may not entirely be due to simple quantization effects (Xu *et al* 1992; Zheng *et al* 1992b; Narasimhan *et al* 1993). Other experiments also provided sufficient reasons to believe that the luminescence in PS may arise due to different silicon compounds like  $\alpha$ -Si:H (Wolford *et al* 1983), polysilane (Furukawa and Matsumoto 1985), silicon hydrides (Prokes *et al* 1992a; Tsai *et al* 1992a, b) and siloxene (Brandt *et al* 1992), deposited as a tissue layer on the vast internal surfaces of the basic PS network. Extensive use of infrared

(IR) absorption spectroscopy has shown Si, H and O to be the only chemical constituents of PS. This has been further confirmed by secondary ion mass spectroscopy (SIMS) (Canham *et al* 1991) as well as X-ray photoelectron spectroscopy (XPS) (Oswald *et al* 1993). To correlate the light emission with the presence of different Si-H or Si-H-O species in PS, controlled chemical alteration of PS layers was utilized (Nakajima *et al* 1992; Ookubo *et al* 1992; Stutzmann *et al* 1992; Lavine *et al* 1993; Robinson *et al* 1993). More recently, it has been shown that the luminescence intensity can be strongly influenced by changing the surface chemistry (Banerjee *et al* 1994), although the enhancement could not be correlated to any chemical species (particularly hydrides or siloxene) conclusively. Using Raman spectroscopy together with IR spectroscopy (Banerjee *et al* 1992; Tischler and Collins 1992; Banerjee *et al* 1994) and by soft X-ray luminescence (Sham *et al* 1993), it has been shown that the luminescence in PS is unlikely to be related to siloxene, despite the striking similarity between the PL, IR absorption and Raman spectra of both the materials. Since the emission process is strongly related to the electronic band structure, a better understanding of PL behaviour may be obtained by direct absorption measurements on free-standing PS layers (Sagnes *et al* 1993; Xie *et al* 1993). However, the results depend strongly on the estimation of the effective volume of the absorbing medium, which is a nontrivial proposition. Alternatively, several groups have tried to understand the excitation processes by using photoluminescence excitation (PLE) spectroscopy on PS layers on silicon substrates (Motohiro *et al* 1991; Wang *et al* 1993; Sinha *et al* 1994) as well as on free-standing PS layers (Stutzmann *et al* 1993). All these experiments highlight two important properties of porous silicon, viz. the absorption edge of PS is significantly blue-shifted with respect to crystalline silicon and relative absorption closer to the peak emission energies is very small. In this paper results of IR absorption, PL and PLE experiments performed on freshly prepared and chemically treated (for surface modification) PS samples in TIFR will be reviewed. From all these experiments it is inferred that (a) the luminescence in PS is unlikely to be arising due to a chemical complex of silicon, hydrogen and/or oxygen, although chemical alteration of surface plays a very important role in changing the luminescence behaviour, and (b) the absorption and emission process is similar to that of a disordered material (like a-Si:H) modified by the quantum nature of this material.

## 2. Experimental

The PS samples for this study were made by anodization of 15–30  $\Omega$ -cm p-type silicon in 48% HF with a current density of 10–20 mA/cm<sup>2</sup> in a double-tank cell, schematically shown in figure 1. Both sides of the substrates were polished to facilitate IR measurements. Typical thickness for  $\sim$  30–40 min anodized samples is between 5 and 10  $\mu$ m. It is difficult to measure the exact thickness by cross-sectional scanning electron microscopy (XSEM) due to the porous nature of the material. The PL measurements were performed in vacuum ( $\leq 10^{-3}$  torr) to avoid photoinduced degradation of the PL intensity (Tischler *et al* 1992). The samples were placed in a closed-cycle helium cryostat to vary the temperature between 10 K and 293 K for PL and PLE measurements. The experimental set-up consisted of an argon ion laser (488 nm line) as the excitation source, a 0.67 m grating monochromator for dispersion of the PL signal and a Si p-i-n photodiode with a lock-in amplifier as the detector.

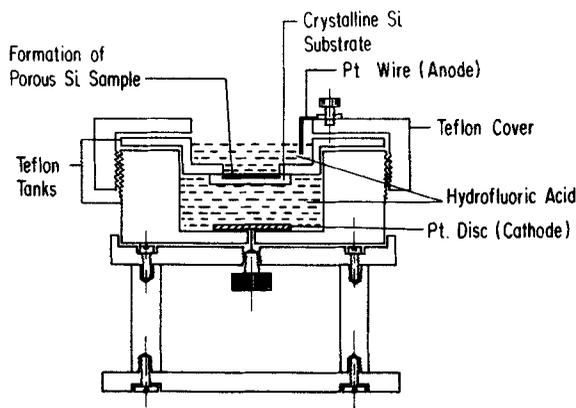


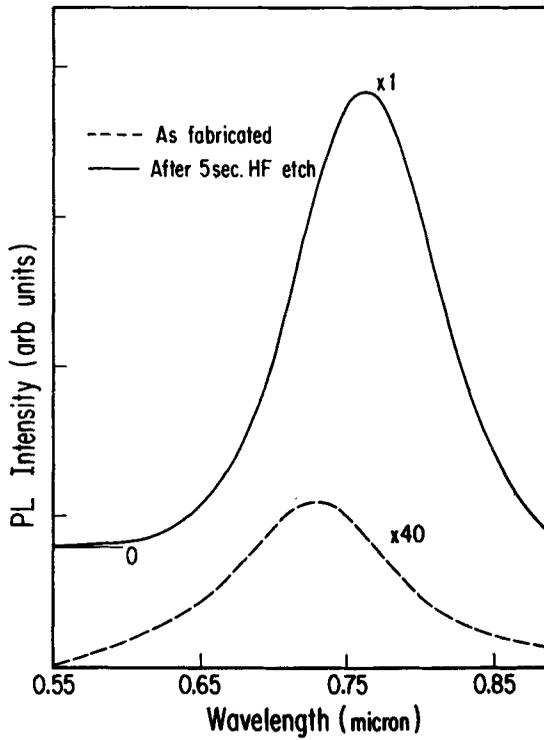
Figure 1. Schematic drawing of double-tank silicon anodization cell.

IR measurements in the  $400\text{--}4000\text{ cm}^{-1}$  range (with a resolution of  $8\text{ cm}^{-1}$ ) were performed using a Biorad FTS45 series Fourier transform infrared (FTIR) spectrometer in a dry nitrogen ambient. A variable-energy photon source using a 150 W halogen lamp with a 1/8 metre monochromator was used as the excitation source for the PLE measurements. The excitation source, including the monochromator and associated optics, was calibrated using a thermopile detector placed at the sample position. A second 1/8 metre monochromator was used to select different emission energies (detection energies) in conjunction with an S20 photomultiplier and lock-in amplifier to detect the emission signal as a function of photon energy of the excitation source. The photomultiplier signal was normalized with respect to the excitation flux to obtain the PLE signal. All the samples were first characterized for their PL and IR behaviour after fabrication. Prior to further chemical treatments of the PS layers, all the samples were subjected to a brief etching in HF (5–10 sec) in order to remove any residual surface oxide that may grow during the fabrication or measurements.

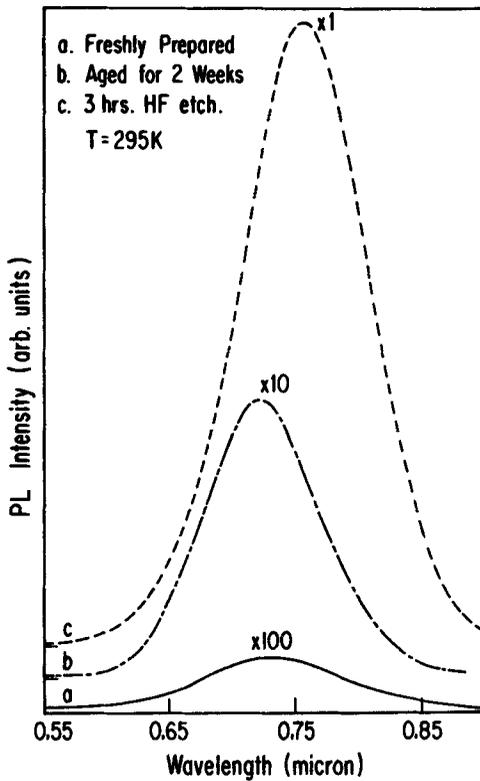
### 3. Results

#### 3.1 Photoluminescence emission

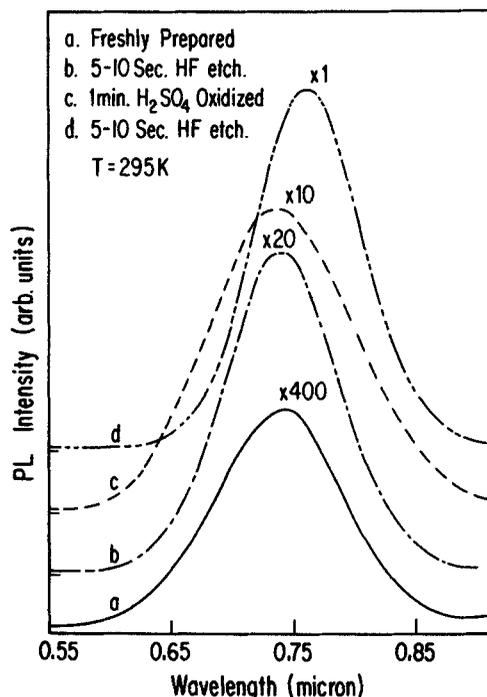
A typical PL spectrum of a freshly anodized sample is shown in figure 2. The PL emission peak is between  $0.7$  and  $0.8\ \mu\text{m}$  and the intensity is usually low in as-fabricated samples and varies to a significant extent in different samples. By etching the PS layer in HF for 5–10 sec the intensity of emission increases by  $\sim 10\text{--}40$  times (depending upon the initial intensity) with a significant red shift in the emission energy. After aging for about two weeks under normal laboratory ambient, the PL intensity shows a factor-of-10 enhancement without any appreciable shift in the emission energy as shown in figure 3(a and b). After chemically etching (without any current flow) the sample in HF for 3 h, a further enhancement in PL intensity is observed together with a significant red shift in the emission energy (figure 3c). In order to further investigate the role of quantization, a sequence of chemical treatments



**Figure 2.** Photoluminescence spectra of freshly prepared PS and after surface oxide removal by 5–10 sec HF etching.



**Figure 3.** Photoluminescence spectra of PS: (a) freshly prepared, (b) after two weeks aging and (c) after 3 h HF etch (Banerjee *et al* 1994).



**Figure 4.** Photoluminescence spectra of PS: (a) freshly prepared, (b) after 5–10 sec HF etch, (c) after oxidation in sulphuric acid and (d) after oxide removal by 5–10 sec HF etching (Banerjee *et al* 1994).

was designed such that the size of the silicon columns could be reduced in small steps of  $\sim 2$  nm by chemical oxidation in sulphuric acid and subsequent removal of oxide by a brief (5–10 sec) etching in HF. An additional advantage of this chemical etching sequence is that the silicon surface can be terminated by oxide or hydride(s). Figure 4 shows a set of PL spectra of freshly prepared PS layer and after the chemical treatment sequence described earlier. A comparison of spectra a and b in figure 4 (measured after removing the residual oxide from the freshly prepared sample prior to chemical oxidation) shows a very significant enhancement in the PL intensity with practically no shift in the emission energy. Further enhancement in the PL intensity is observed by chemical oxidation in sulphuric acid (spectrum c). Small or no blue shift in the emission energy is observed although the full width at half maximum (FWHM) of the PL spectrum is increased appreciably. By removing the oxide in HF the PL intensity increases further (spectrum d). However, there is a substantial red shift observed after this step.

### 3.2 Infrared absorption

To investigate the other alternative of chemical origin of luminescence, IR absorption spectra of the PS samples described in the previous paragraph were also measured. The IR absorption spectra for the samples shown in figures 3 and 4 are shown in figures 5 and 6 respectively. Since the contribution from the substrate was found to

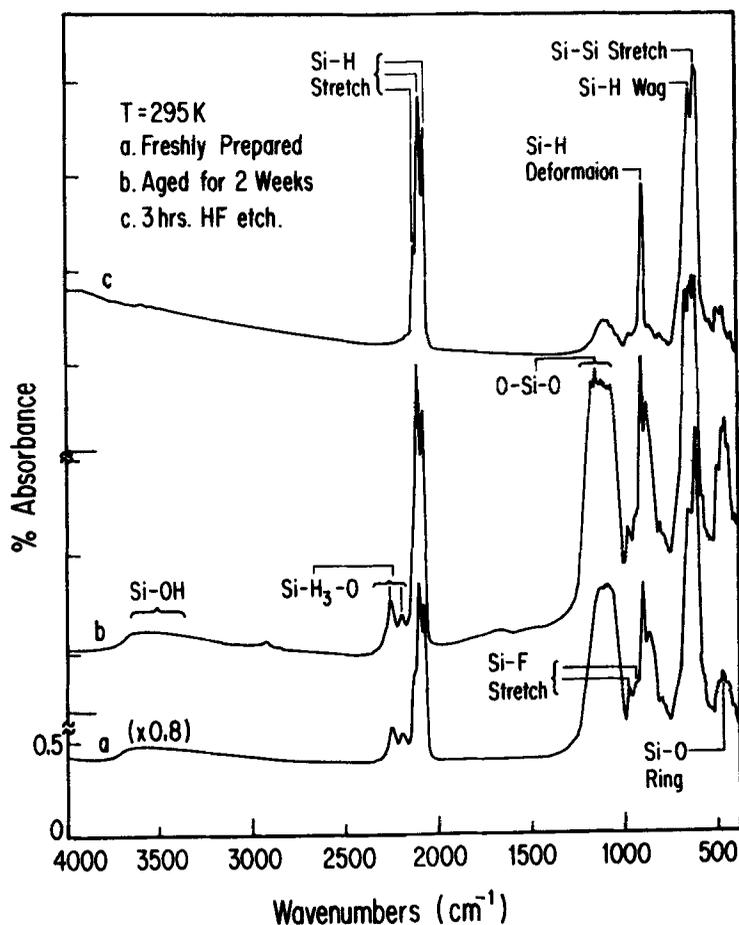
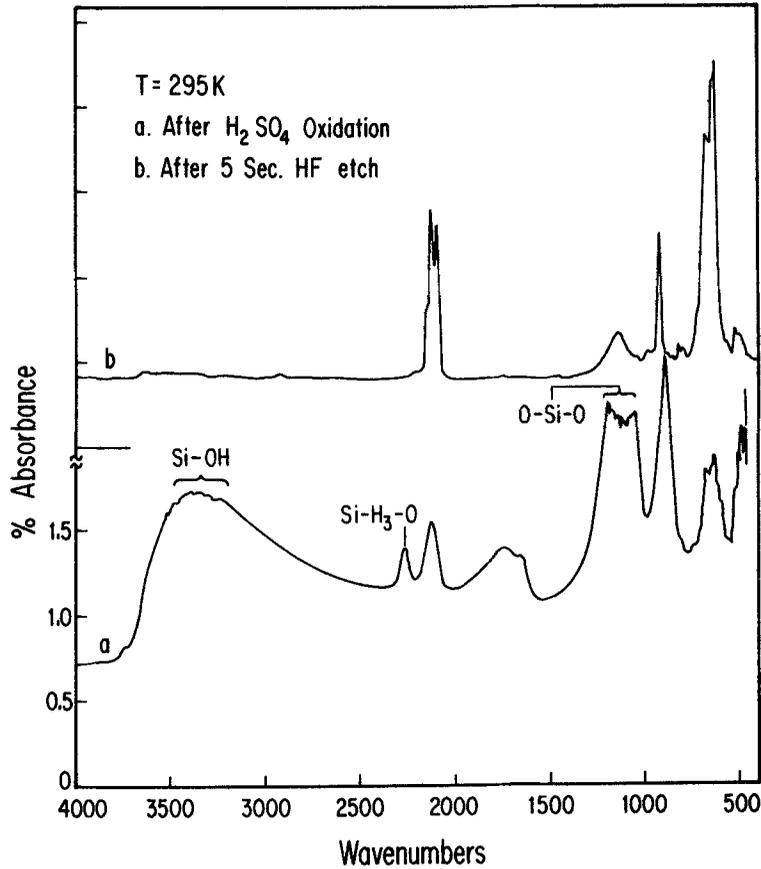


Figure 5. Infrared absorption spectra of PS: (a) freshly prepared, (b) after two weeks aging, (c) after 3 h HF etch. Major vibration modes are indicated (Banerjee *et al* 1994).

be negligible, the data presented here have not been corrected for substrate effects. The major vibrational features observed are quite similar to those reported earlier (Brandt *et al* 1992; Nakajima *et al* 1992; Ookubo *et al* 1992; Stutzmann *et al* 1992; Tsai *et al* 1992a; Lavine *et al* 1993; Robinson *et al* 1993). However, the components are much better resolved in the spectra shown here. There are five major groups at  $425\text{--}470\text{ cm}^{-1}$ ,  $615\text{--}665\text{ cm}^{-1}$ ,  $800\text{--}1000\text{ cm}^{-1}$ ,  $1165\text{--}1175\text{ cm}^{-1}$ ,  $2080\text{--}2250\text{ cm}^{-1}$ , and a very broad band centred around  $3500\text{ cm}^{-1}$  in all the spectra except c in figure 5 and b in figure 6, which have only three major features. The IR spectrum of a PS layer oxidized in sulphuric acid is shown in a of figure 6. The intensities of the group at  $1070\text{--}1170\text{ cm}^{-1}$  and the broad band at  $3500\text{ cm}^{-1}$  were found to increase significantly. A new band centred around  $1700\text{ cm}^{-1}$  appears after oxidation. It should be noticed that the spectral features are not as sharp compared to the spectra shown in figure 5. The identification of these IR absorption features of PS has recently been reviewed (Banerjee *et al* 1994).



**Figure 6.** Infrared absorption spectra of PS: (a) after oxidation in sulphuric acid and (b) after oxide removal by 5–10 sec HF etching (Banerjee *et al* 1994).

### 3.3 Temperature dependence of PL

Temperature dependence of PL emission energy and integrated intensity can provide useful information about the emission mechanism(s). The PL spectra as a function of temperature between 10 K and 293 K are shown in figure 7. The most remarkable feature of these spectra is the large (reversible) blue shift observed in the emission energy at temperatures above 100 K. A sudden enhancement in the width of the emission spectra at 140 K points to the fact that there are more than one component to the PL emission. The peak as well as the integrated PL intensity and emission energy at any temperature are therefore subjected to the relative magnitudes of the individual components and may be very different in different samples. A Gaussian decomposition of the PL spectra (Narasimhan *et al* 1993) on a very large set of samples indicates that the PL spectra indeed have at least three components with different temperature dependencies and the behaviours of the individual components are schematically shown in figure 8.

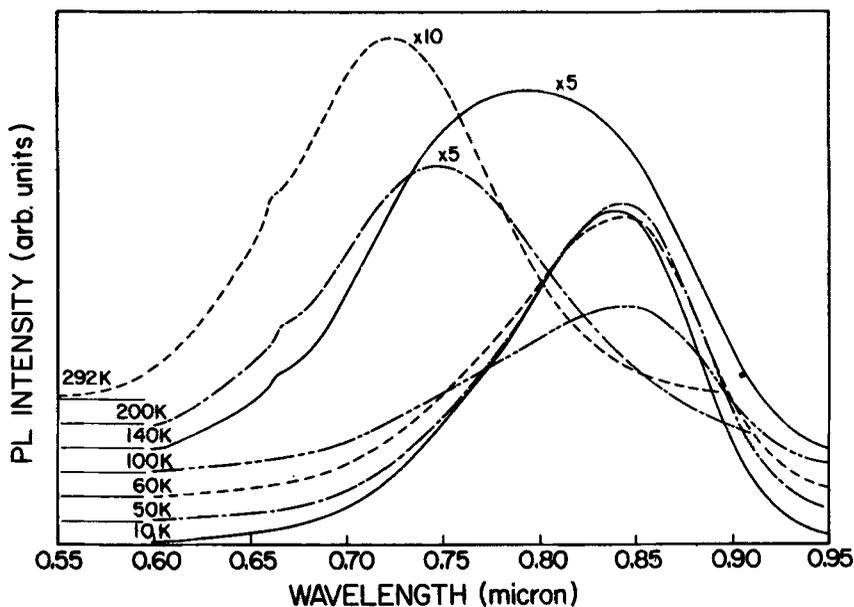


Figure 7. Temperature dependence of PL spectra between 10 K and 293 K (Narasimhan *et al* 1993).

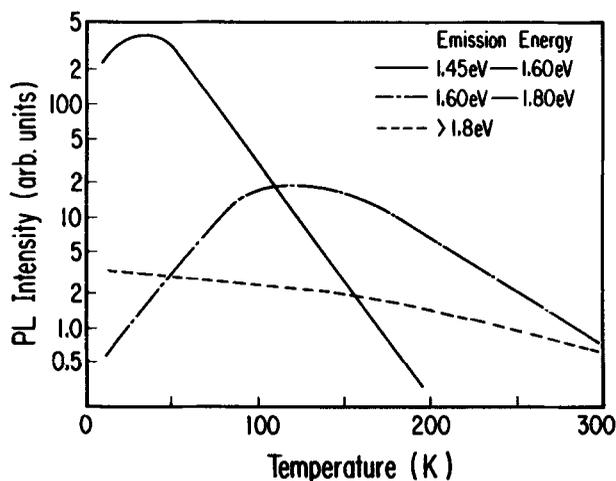


Figure 8. Schematic temperature dependencies of the three PL components. The inset shows the typical energy range of each component.

### 3.4 Photoluminescence excitation spectroscopy

Since emission processes are strongly dependent on the excitation processes, a better understanding of emission processes can be obtained by identifying the interdependence of the two processes. Typical PLE spectra at room temperature (293 K) for PS samples at a few different detection (emission) energies ( $E_d$ ) are shown in figure 9. The peak of each PLE spectrum ( $E_p$ ) is significantly higher than  $E_d$ . It is also

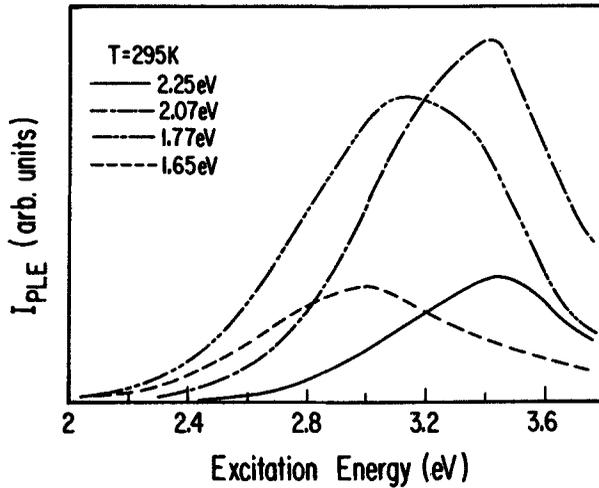


Figure 9. Room-temperature PLE spectra of PS layers at different detection energies  $E_d$  (Sinha *et al* 1994).

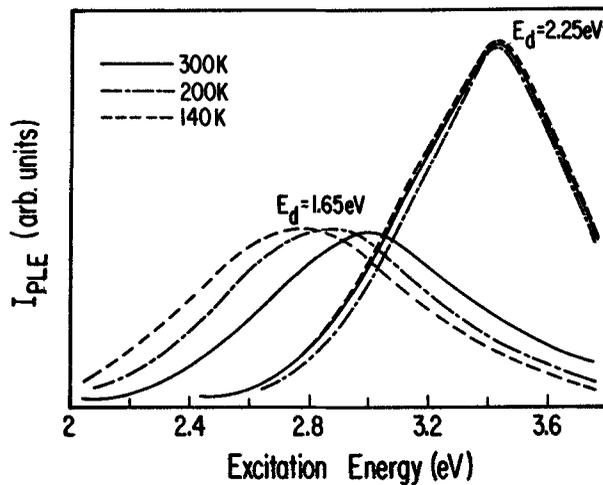


Figure 10. Low-temperature PLE spectra at 293 K, 200 K and 140 K for  $E_d = 1.65$  eV and 2.25 eV (Sinha *et al* 1994).

observed that ( $E_p$ ) increases for higher  $E_d$  and saturates at  $\sim 3.35$ – $3.4$  eV for  $E_d \geq 2.07$  eV. The PLE spectra for two different  $E_d$ , 1.65 eV and 2.25 eV (for clarity), at 293 K, 200 K and 140 K are shown in figure 10. The spectra are normalized for comparison such that their peak strength at each  $E_d$  is the same at all temperatures. It is obvious that for  $E_d = 2.25$  eV the PLE spectra look similar (except for the scaling factor) at all temperatures, whereas for  $E_d = 1.65$  eV the spectra shift to lower  $E_p$  values at lower temperatures. The variation of  $E_p$  as a function of temperature is linear for all  $E_d$  and has been shown in figure 11. However, the slope of the lines decreases as  $E_d$  increases and practically goes to zero.

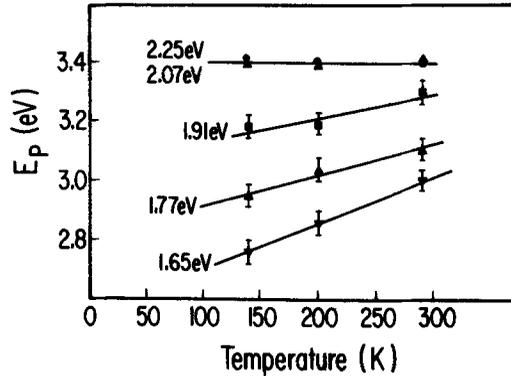


Figure 11. Temperature dependence of peak excitation energy  $E_p$  for different  $E_a$  values (Sinha *et al* 1994).

## 4. Discussion

### 4.1 Quantization as origin of luminescence

The variation in PL emission energy and intensity mentioned in § 3.1 in as-fabricated PS samples is mainly due to the inhomogeneous nature of PS material. These inhomogeneities result from the microscopically non-uniform silicon dissolution process and are difficult to control, although the reason for such microscopic inhomogeneities are very well understood (Smith and Collins 1992; Bomchil *et al* 1993). Since silicon dissolution in HF is basically an oxidation process (Lehmann and Gösele 1991), it is not surprising that there is significant amount of residual oxide (shown in the IR absorption spectra of figure 5a) in as-fabricated sample. The enhancement in PL intensity after a brief etching in HF (to remove surface oxide) can be attributed to better hydrogen passivation compared to the as-fabricated sample; however, the red shift in the emission energy is not easy to explain as a simple consequence of quantization. It is also not clear whether the surface oxidation is positively detrimental because PS samples after aging in normal laboratory ambient (figure 3b) and chemically oxidized PS (figure 4c) show higher intensity. In fact other oxidation experiments also claim that oxidation results in higher intensity and better stability (Petrova-Koch *et al* 1992; Shih *et al* 1992; Xiao *et al* 1993). The large enhancement in PL intensity observed (figure 3c) after extended passive etching in HF for 3 h may point to increased oscillator strength due to reduction in nanocrystallite sizes. However, if quantization were to be the only dominant mechanism responsible for the luminescence in PS, a blue shift in emission energy would be expected, which is contrary to the observed red shift. It is well known that extended chemical etching in HF reduces the size of the silicon nanocrystallites significantly. In fact it has been observed that etching PS for longer durations (4 h or more) in HF results in partial or total collapse of the PS network causing reduction in PL intensity. The data in this situation are unreliable for further analysis.

The reduction in nanocrystallite sizes of the PS network can also be achieved in small steps by chemically oxidizing silicon in sulphuric acid to form silicon oxide at the walls of the basic PS network. Chemical oxidation is a self-arresting process

( $\sim 1$ – $2$  nm oxide grows at room temperature) and ensures that the bulk of the material is not affected. This treatment also results in a surface passivated with oxide instead of hydrogen. Although PL intensity was enhanced approximately by a factor of 10, there was no significant blue shift (figure 4c) as expected in view of the quantization theory of PL emission. In fact it is very difficult to establish any definite trend regarding the blue shift in the emission energy over a very large set of samples. Similar results were obtained by anodic oxidation and chemical oxidation in hydrogen peroxide. It has been shown earlier (Narasimhan *et al* 1993) that a high-energy contribution can be selectively enhanced after oxidation causing an enhanced width and/or an overall blue shift in the PL spectra. In some weakly luminescent samples this high-energy contribution was found to be dominant after prolonged etching in HF (Banerjee *et al* 1992). It is likely that the slight blue shift often observed after oxidation could also result from stress in the films (Prokes *et al* 1992b). Using fluorescence microscopy we indeed observe that the microstructure of oxidized PS changes from a smooth to a parched-earth texture. In addition the colour changes from dark red-orange to yellow or yellow-green depending upon the extent of oxidation. By dissolving the oxide by a brief (5–10 sec) etch in HF, hydrogen can be restored at the surface without altering the sizes of the silicon nanocrystallites (the dissolution rates of silicon dioxide and silicon in HF are  $\sim 1:100$ ). It is evident from figure 4 that an overall enhancement in PL intensity of  $\sim 2$ – $3$  orders of magnitude can be easily achieved as a result of the entire sequence of chemical treatments. However, contrary to the expected blue shift in the emission energy, a significant red shift is observed at the end of the chemical etching sequences (figure 4), in particular after HF etching of PS layers (figures 2 and 3). These observations highlight two very important properties of luminescence in PS: (a) PL cannot be simply attributed to effect of quantization and (b) chemical treatments play a very important role in changing the PL intensity by very large amounts.

#### 4.2 Chemical complex(es) as source of luminescence

The IR absorption spectra shown in figures 5 and 6 indicate that Si, H and O are the only chemical constituents of PS. The most easy to interpret are the well-resolved Si–H vibration modes in figures 5c and 6b. The most intense are the Si–H stretch modes at  $2000\text{ cm}^{-1}$  and  $2110\text{ cm}^{-1}$  with a shoulder at  $2140\text{ cm}^{-1}$ . A more clear understanding of these assignments can be obtained from the Si–H deformation (bending) modes observed between  $800$  and  $1000\text{ cm}^{-1}$ . The most prominent Si–H deformation mode present in these spectra (figures 5c and 6b) is a very sharp peak at  $910\text{ cm}^{-1}$ . The other prominent absorption features at  $630$  and  $615\text{ cm}^{-1}$  are related to wag mode of Si–H and stretch mode of Si–Si respectively. These spectra resemble closely that observed in different amorphous Si–H compounds and a more rigorous assignment of these bands has been recently summarized (Banerjee *et al* 1994). From a comparison of the spectrum in figure 5a with those in figure 6, the absorption bands at  $425$ – $470\text{ cm}^{-1}$ ,  $1070$ – $1150\text{ cm}^{-1}$ , and a broad band centred around  $3500\text{ cm}^{-1}$  are identified to be due to oxygen. The intensities of these bands show significant enhancement upon aging (figure 5b) as well as after oxidation in sulphuric acid (figure 6a). This is usually accompanied by significant widening of the absorption bands, probably due to the structural changes or/and stress effects in the PS layers. The fact

that these bands almost disappear after etching the PS layer in HF (figures 5c and 6b) further supports their origin to be oxygen. Similar behaviour has been observed for the doublet at  $2190\text{--}2250\text{ cm}^{-1}$ ; therefore we infer that this absorption feature is also related to oxygen. The large enhancement in the intensity of  $3500\text{ cm}^{-1}$  band upon oxidation in sulphuric acid indicates that presence of hydroxyl group is important for the oxidation of PS and presumably oxidation proceeds through OH groups attached to the silicon skeleton. This explains the significant oxide growth upon aging the samples (figure 5b) in ordinary laboratory environment in agreement with the mechanism of oxidation reported (Beckmann 1965; Canham *et al* 1991). The large change in the IR spectra after oxidation also indicates that a very large fraction of IR absorption is taking place at the surface, contrary to the belief that IR probes deeper into the bulk compared to PL. It must be remembered that the PS surface is a very significant fraction of the effective absorbing medium. However, it is difficult to comment on the volumes probed by the two techniques in this case.

The analysis of the results described here can be summarized with the following comments on the correlation of the PL and IR absorption experiments. From the PL spectra shown in figure 3 it is obvious that the emission intensity increases by about two orders of magnitude after passive etching the sample in HF for an extended period. However, enhancement in the intensities of all the hydride-related IR absorption is  $\leq 10\%$  which is not proportional to the observed change in the PL intensity. Furthermore, the Si-H-related IR absorption does not show any significant change (in terms of line shape, width, etc.) after passive HF etching. It therefore implies that the changes in the PL spectra as a result of chemical etching are not directly related to silicon hydride species. Similar conclusions were drawn by removing hydrides by carbon tetrachloride (Lavine *et al* 1993) and from other passive HF etching experiments (Robinson *et al* 1993). The PL intensity also shows an enhancement after chemical oxidation (figure 4c). It should be noted that the intensities of the oxygen-related bands including the one at  $425\text{--}470\text{ cm}^{-1}$  in the IR spectrum (figure 6a) increase appreciably. This band has been associated with chain or cyclic structures of Si and O (Beckmann 1965; Stutzmann *et al* 1992), which are the basic structural element of compounds like siloxene. However, further enhancement in the PL intensity is observed with simultaneous reduction in the  $425\text{--}470\text{ cm}^{-1}$  band as well as the other oxygen-related bands in the IR spectra. It is therefore difficult to comprehend that oxygen-related compounds such as oxides or siloxene are directly responsible for the observed PL behaviour. This observation is in agreement with the Raman spectroscopy results (Banerjee *et al* 1992; Tischler and Collins 1992) and more recent soft X-ray luminescence results (Sham *et al* 1993). Thus a few very important conclusions could be drawn from the discussion so far: (a) PS surface terminated with hydrogen results in most intense luminescence in  $0.7\text{--}0.75\text{ }\mu\text{m}$  range, (b) the PL intensity is very sensitive to the chemical changes at the surface and (c) there is no direct evidence of any particular chemical species responsible for the luminescence.

#### 4.3 Anomalous temperature dependence of PL

For a normal semiconductor it is expected that the optical emission energy increases upon lowering the sample temperature. The anomalous red shift observed in the emission energy (figure 7) on lowering the sample temperature is indeed quite

intriguing. Such large shift in the emission energy can only be explained if the emission is a multicomponent process with different mechanisms operative at different temperatures. From figure 7 it is clear that there are at least two components in the PL spectrum of PS. Due to the different relative magnitudes of these components, their large intermixing and different temperature dependencies, it is not always possible to clearly identify and understand their exact behaviour. This is also precisely the reason for a wide variety of temperature-dependent behaviour of PL reported in the literature (Xu *et al* 1992; Zhang *et al* 1992b). It has been pointed out (Narasimhan *et al* 1993) that the PL spectrum has at least three components. From a Gaussian deconvolution of PL spectra of a large set of samples (with predominantly a single component between  $\sim 10$  K and 200 K) the following comments can be made regarding the relative temperature dependencies of these components shown in figure 8. The lowest-energy (1.45–1.6 eV) component is very intense at low temperature and decays very rapidly above 60–80 K. This behaviour is similar to the luminescence band observed in a-Si:H (Street 1984). The intermediate-energy (1.6–1.8 eV) component (roughly a factor of 5 less intense in terms of peak values) has maximum intensity at  $\geq 150$  K and falls on either side of this temperature. The highest-energy ( $\geq 1.8$  eV) component is usually the least intense and is relatively independent of temperature in the entire temperature range. From the above discussion it is also quite clear that the activation energies determined from the temperature dependence of peak or integrated PL intensity can be non-unique and may not represent a single mechanism.

#### 4.4 Excitation processes in PS

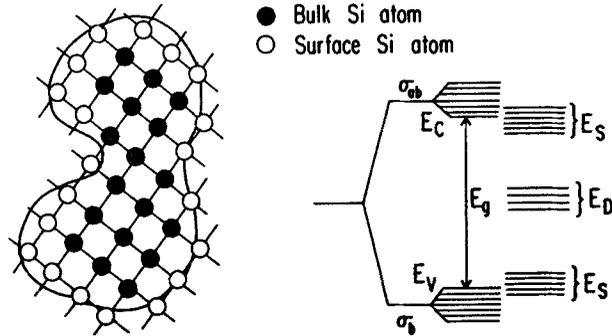
It is clear from the above discussion that it is not really possible to isolate the different emission processes in energy and temperature. The PLE measurements provide some insight into the interdependence of the excitation and the emission in the PS system. The PLE spectra at room temperature (figure 9) clearly show that significant excitation begins only above 2 eV and the peak excitation energies are shifted to much higher values compared to the peak emission energies. This points to the fact that there is significant energy lost between the excitation and emission, possibly due to the relaxation of carriers to the lower-lying emission states. From the temperature-dependent PLE results shown in figure 10 it can be inferred that there are at least two different processes contributing to the PL emission—one leading to the emission at higher energies  $> 2$  eV while the second and the dominating process contributing to the emission at energies  $< 2$  eV. Although it is not possible to isolate these two emission bands distinctly in the PL spectra presented here, presence of a very weak high energy band with a peak at  $\sim 2.4$  eV has been reported (Calcott *et al* 1993). The excitation process contributing to the high-energy emission is relatively independent of the emission energy  $E_d$  as well as temperature and possibly is intrinsic to the PS structure. This emission probably arises from a set of well-defined, homogeneously broadened electronic states similar to that in small clusters or molecular complexes (Koch *et al* 1993; Sinha *et al* 1993). This model is consistent with the smaller decay time constant for the high-energy part of the PL spectra observed in transient-PL experiments (Andrianov *et al* 1992).

The excitation process responsible for the emission at lower energies ( $< 2$  eV) is strongly dependent on  $E_d$  and temperature. The first feature is reflected in the strong

dependence of emission energy on the excitation energy and is very typical of disordered systems like a-Si:H (Street 1984). However, additional effect of very small sizes of the crystallites and network-like structure of PS play a very significant role in modifying the energy and time scales of the relaxation processes observed in PS compared to a-Si:H. In a simplified model, PS can be visualized as a distribution of irregular nanocrystallites with different sizes. Carriers in such a highly disordered material experience severely perturbed fluctuating potential surfaces. The optical excitation can take place at all points in this fluctuating potential surface (depending upon the excitation energy), however, the emission takes place only from the local minima. This is manifested in the large difference in  $E_p$  and  $E_d$  observed in figure 9. Assuming rapid thermalization of holes as in case of a-Si:H (Tiedje and Rose 1980), the relaxation of electrons to these local minima occurs through multiple trapping (MT) process involving thermal emission, transport and capture of carriers through the distribution of localized energy states. After the initial excitation, the carriers tend to slowly thermalize to deeper and deeper localized states before recombining radiatively (Sinha *et al* 1994). Therefore the peak of PL emission progressively shifts to lower energies with increasing time delay after the initial excitation. At low temperature this relaxation process is slower due to the reduction in thermal energy of the carriers. As a result  $E_p$  decreases linearly with temperature as shown in figure 11. However, as  $E_d$  increases the slope of the lines decreases tending towards zero for higher  $E_d$  values. This discussion emphasizes a very significant aspect of the nature of optical excitation and emission process in PS, i.e. the nanocrystallite nature of the material plays a key role. Using X-ray measurements Barla *et al* (1984) showed that the basic crystalline nature of silicon is preserved in PS. This is further supported by the experimental evidence of optical phonon participation in PL emission (Calcott *et al* 1993; Suemoto *et al* 1993). It has also established that nanocrystallite silicon particles fabricated by nonelectrochemical techniques also exhibit the novel luminescence behaviour observed in PS (Takagi *et al* 1990; Hummel and Chang 1992; Rückschloss *et al* 1993; Saunders *et al* 1993).

## 5. Towards a unified model

From the evidences and arguments presented here, it is beyond doubt that nanocrystallinity and surface effects play equally important roles in luminescence of PS. Therefore it is imperative to invoke a more comprehensive model involving the quantization effect and the role of surfaces. From the temperature dependence of PL and PLE measurements it is obvious that there are different mechanisms involved in excitation as well as emission. Based on the experimental results obtained so far, it is only possible to state that the emission at higher energies is more intrinsic in nature whereas the lower-energy emission, also the more dominant one, is disorder-related showing a more complex behaviour. In order to understand the effect of disorder in a simplified way one can look at a silicon nanocrystallite as an isolated entity as shown in figure 12. It is known that the anodization process leading to PS formation gives rise to irregular shapes of nanocrystallites with a certain size distribution. From a simple tight-binding approximation it is known that the band gap  $E_g$  of crystallites would depend on their sizes as has been shown in several theoretical calculations by assuming one-dimensional wire model for PS (Buda *et al* 1992; Ohno *et al* 1992; Read *et al* 1992; Sanders and Chang 1992). As a result, carriers



**Figure 12.** Schematic picture of a silicon nanocrystallite and the energy band diagram including the effect of surface states.  $E_g$  (function of crystallites size) is the band gap energy arising due to the volume (bulk) states, and  $E_D$  deep levels and  $E_S$  shallow levels arising due to the surface states.

will experience a fluctuating-potential environment with no fixed periodicity within a nanocrystallite as well as throughout the volume of the PS layer. It has been shown in this paper that this simple model of disorder in PS is adequate to understand many of the results of PL and PLE experiments in a comprehensive manner.

However, it is also important to realize that the number of silicon atoms which are abruptly terminated at the surface is a significant fraction of the total number of silicon atoms in the crystallites (figure 12). In general, these surface silicon atoms give rise to surface states due to dangling bonds similar to those observed in a-Si:H. The surface silicon atoms of the individual nanocrystallites tend to reorganize themselves in order to lower the stress and total energy. In this process the energies of the surface states are modified according to the local chemical environment such as termination of bonds by H or O etc. available for passivation. Due to their irregular shape it is not really possible to completely passivate all the dangling bonds of the surface silicon atoms. Clearly, in a real situation, these states may reside as deep levels  $E_D$  or shallow levels  $E_S$  (figure 12). Due to the distribution of crystallite sizes the effective band gap of the material changes throughout the volume of the PS layer. Therefore the relative energies of the surface states are not uniform throughout the material. Individual levels particularly the shallow ones may be degenerate with the band edges. A combined effect of all these factors provides additional sources of potential fluctuation throughout the entire volume of the PS layer. This presents a large number of possible distributions of energy states depending upon the size distribution and chemical environment of the nanocrystallites. The radiative and non-radiative recombination may occur via bulk (volume) states or by localization of one or both the types of carriers in these shallow and deep surface states. In this framework, it is possible that in the process of reducing the size of the nanocrystallites the whole distribution of the energy levels may change in quite an unpredictable manner. As a result, reduction of crystallites sizes may not produce the blue shifts in the emission energy expected from purely size considerations. Furthermore, it is also likely that the efficiency of different mechanisms contributing to the PL are affected differently by such (hard to predict) reorganizations. It is therefore probable that the effect of chemical etching sequence reported in this paper shows shifts in the emission energies which are not in agreement with a simple model of size reduction

of the nanocrystallites. In fact this model integrating the effects of nanocrystallite silicon with surface states (smart quantum model) has been utilized to explain some of the observed 0.8 eV infrared emission, band gap change with porosity, and different time responses of the different visible emission peaks (Koch *et al* 1993).

## 6. Conclusions

A wide variety of spectroscopic techniques have been used to understand the mechanism(s) responsible for the intense luminescence observed in PS between 0.7 and 0.75  $\mu\text{m}$ . The shifts in the PL emission energy together with the enhancement in the PL intensity as a result of passive HF etching as well as chemical oxidation and subsequent removal of oxide cast doubts on a simple quantization model to be the origin of luminescence. The chemical oxidation and oxide removal experiments could not establish a direct relation of the luminescence in PS to oxygen-related compounds such as siloxene. The enhancement in the PL intensity (0.7–0.75  $\mu\text{m}$  range) by hydrogen termination of PS surface is striking. However, the oxide removal experiments and the passive etching experiments indicate that a better hydrogen passivation may not be entirely responsible for the enhancement in the PL intensity because an equivalent change in hydride absorption spectra was not observed. Nevertheless, these results consolidate the contribution of surface effects in enhancing the luminescence intensity. The temperature dependence of excitation as well as emission are shown to be multicomponent in nature. This multicomponent emission behaviour is responsible for the anomalous temperature dependence of PL intensity and emission energy. A better understanding of PL emission processes comes from the PLE experiments which indicate that the higher-energy part of the PL emission may be an intrinsic process, whereas the more dominant lower-energy emission in 0.7–0.75  $\mu\text{m}$  range is related to disorder. These experiments also highlight the nanocrystallite nature of PS as the essential aspect of light emission. Most of the experimental results could be explained very well by integrating the role of surface effects with the quantum size model. However, at this stage it is still not possible to unravel the complete band structure of porous silicon. Although significant contribution has been made in uncovering some of the important aspects of luminescence in PS, many questions still remain to be addressed. Some of the future challenges in this field of research include the effective band structure, nature of optical transitions, electron injection and transport and most of all the suitability of this material for efficient and stable optoelectronic application.

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