

## **The photoluminescence of porous silicon**

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### **A.1 Characteristics of photoluminescence**

Photoluminescence (PL) from porous silicon is observable at wavelengths ranging from the ultra-violet<sup>[1]</sup> to the infrared. The PL is usually excited by a wavelength shorter than the emission wavelength, with excitation wavelengths typically lying between 260nm (for ultra-violet emission) and approximately 520nm<sup>[2]</sup>. Alternatively, PL can be excited through an up-conversion process by pumping the porous silicon at infrared wavelengths<sup>[3,4]</sup>.

The characteristics of the PL change as the wavelength of emission changes from ultraviolet wavelengths to infrared wavelengths. A specific characteristic normally applies to a discrete set of wavelengths and has resulted in a grouping of wavelengths into three bands to describe these characteristics. The main characteristics of each of these wavelength bands, called the 'red', 'blue' and 'infrared' bands are given in Tables A-1, A-2 and A-3.

The PL from porous silicon in its as-anodised form is in the 'red' band and may also exhibit a second peak in the 'infrared' band<sup>[5]</sup>. The PL of the 'blue' band is obtained when the sample contains a large amount of oxygen<sup>[25]</sup> which has been achieved by oxidation<sup>[6]</sup>, rapid thermal oxidation (RTO)<sup>[14]</sup>, spark-erosion<sup>[7]</sup> or the exposure to boiling water<sup>[8]</sup>. Such treatment does not always cause porous silicon to photoluminesce at shorter wavelengths<sup>[16]</sup>, and the transfer between the 'red' and 'blue' band PL is not a continuous variation but rather a switching between the two wavelengths.

### **A.2 Mechanisms for photoluminescence**

The mechanism for PL from porous silicon has been the cause of much debate since room temperature PL was first demonstrated in 1990<sup>[2]</sup>. Since this time approximately 50% of the publications concerning porous silicon have addressed this issue<sup>[9]</sup>. In these articles a range of possible mechanisms for PL have been proposed with other papers either supporting or rejecting these theories in support of another theory. It is now generally agreed, however, that different mechanisms are responsible for the different PL bands described in section A-1.

#### **A.2.1 The 'red' PL band.**

It is the 'red' band PL that has attracted the most attention from researchers trying to elucidate the mechanism for PL in porous silicon. This is because it is the only band to be efficiently electrically excited.

##### **A.2.1.1 Surface species and molecules.**

One possible mechanism for the 'red' band PL is that it is caused by surface hydrides on the branches of the porous silicon<sup>[10]</sup>. Work has shown<sup>[11]</sup> that tuneable visible PL exists that has been attributed to SiH<sub>x</sub> groups. Further evidence for this hydride based hypothesis originated in the observed quenching of the PL when hydrogen is desorbed from the branches of the porous silicon through heat treatment<sup>[12]</sup>. FTIR studies show, however, that the 'red' band PL can be quenched while large amounts of hydrogen remain in the porous silicon<sup>[13]</sup>. It is more likely, therefore, non-radiative dangling bonds, which form when hydrogen is desorbed from the porous silicon, cause the quenching of the PL with temperature<sup>[48]</sup>.

To add further weight against this PL mechanism, porous silicon with a high surface area which, under the proposed mechanism would be expected to photoluminesce with high intensity, instead exhibits no PL<sup>[48]</sup>. Also, the PL intensity can be improved threefold by oxidation which removes hydrogen from the porous silicon<sup>[48]</sup>. It therefore seems reasonable to suppose that surface hydrides do not cause the 'red' band PL in porous silicon. Likewise, that PL exists without the presence of oxygen<sup>[28]</sup> also militates against a surface oxide related mechanism for the 'red' band PL.

- All types of porous silicon show PL if porosity is sufficiently high<sup>[2]</sup>.
- Quantum efficiency of 5%<sup>[22]</sup>
- Generally agreed that silicon crystals required for PL from porous silicon<sup>[14,15,16]</sup>. Jung et al<sup>[17]</sup> suggests crystal structure may only be necessary for the fabrication of PL porous silicon.
- The PL from as-anodised porous silicon shows an increase in the peak wavelength and a decrease in intensity as the excitation wavelength increases<sup>[18]</sup>.
- Peak wavelength decreases as crystal size decreases<sup>[19,20,21]</sup>, though the peak wavelengths of p-type layers are usually longer than for n-type layers<sup>[22, 23]</sup>.
- PL intensity increases and a blue shift with increasing time occurs, by ageing<sup>[14,18]</sup>, chemical dissolution following anodisation<sup>[2]</sup> or photochemical anodisation<sup>[24,25]</sup>.
- Blue shift in peak wavelength for increasing Si-O/Si-H surface bond ratio<sup>[26]</sup>. The PL intensity is unaffected if Si-O bonds are replaced with Si-H bonds (and vice-versa)<sup>[27,28]</sup>.
- Pore environment can quench<sup>[29,30,31]</sup> or enhance<sup>[22]</sup> PL intensity. Level of quenching can depend on surface chemistry<sup>[32]</sup> and may only be partially reversible<sup>[30]</sup>. If particles remain on layer surface and do not enter pores, effect is limited<sup>[29,31]</sup>.
- Maximum intensity observed at  $-73^{\circ}\text{C}$  and is quenched at  $300^{\circ}\text{C}$ <sup>[22]</sup>.
- Decay of PL is either a stretched exponential or non-exponential form, and ranges from  $\mu\text{s}$  decay at room temperature to ms decay at  $4.2\text{K}$ <sup>[32]</sup>.

**Table A-1 Characteristics of the 'red' PL band (approximately 560nm to 860nm)**

- PL can be observed in light-assisted as-anodised porous silicon, but the intensity decays with time and the PL is non-uniform across the anodised wafer<sup>[33]</sup>.
- PL in RTO porous silicon<sup>[34]</sup> and low temperature oxidised porous silicon<sup>[6]</sup> appears through ageing and shows a red shift in the peak intensity with time, together with a widening of the half width of the luminescent band.
- Reproducibility of PL is poor<sup>[33,34]</sup>.
- Quantum efficiency of 0.1%<sup>[22]</sup>
- PL quenched when exposed to methanol<sup>[25]</sup>.
- PL intensity and peak intensity stable under illumination<sup>[33]</sup>.
- Decay of PL is in the ns range<sup>[22,35]</sup> and is independent of both temperature, and the excitation and emission wavelength<sup>[36]</sup>.

**Table A-2 Characteristics of the 'blue' PL band (approximately 400nm to 500nm)**

- PL has a broad spectrum and PL has been observed at wavelengths greater than  $2\mu\text{m}$ <sup>[22]</sup>.
- The relative intensity increases with ageing and, at  $4.2\text{K}$ , can exceed that of the 'red' band<sup>[5]</sup> though is usually weak compared to the 'red' band<sup>[37]</sup>.
- Maximum PL intensity occurs at temperatures around  $350^{\circ}\text{C}$  and is totally quenched at temperatures of around  $450^{\circ}\text{C}$ <sup>[37]</sup>.
- Decay of PL ranges from tens of nanoseconds to  $10\mu\text{s}$  at  $77\text{K}$ <sup>[22]</sup>. These times are generally faster than the decay of 'red' PL at the same temperature.

**Table A-3 Characteristics of the 'infrared' PL band (approximately 900nm to  $2\mu\text{m}$ )**

A variation on the surface species theory is that molecules, specifically siloxene, are responsible for 'red' band PL<sup>[38]</sup>. Under this proposal, molecules are formed as a by-product of the anodisation process and remain on the surface of the porous silicon<sup>[39]</sup>. Siloxene is particularly attractive for the luminescent molecule because, after annealing at 400°C, its own PL properties are similar to those of porous silicon<sup>[48]</sup>. These include PL in the same spectral region as the PL of porous silicon, and infrared absorption spectra which show the same Si-Si, Si-O and Si-H vibration bands as aged porous silicon<sup>[48]</sup>. Also, siloxene shows the same tunability and non-exponential decay of porous silicon, further strengthening the argument for the presence of this material<sup>[39]</sup>. FTIR studies show, however, that as-anodised porous silicon contains no oxygen, implying that no siloxene molecules can be present in this form of luminescent porous silicon<sup>[48]</sup>. Also, during the high temperature oxidation siloxene would decompose, yet porous silicon still luminesces following such treatment<sup>[48]</sup>. It seems unlikely, therefore, that siloxene is responsible for the 'red' band PL.

### A.2.1.2 Hydrogenated porous silicon.

Early structural studies showed that a significant amount of amorphous silicon was contained within porous silicon<sup>[40]</sup>. This knowledge, coupled with the knowledge that visible PL in hydrogenated amorphous silicon (*a*-Si:H) is possible<sup>[41]</sup>, led to the suggestion<sup>[42]</sup> that *a*-Si:H was responsible for 'red' band PL. It was further suggested<sup>[42]</sup> that alloying effects would introduce hydrogen into the amorphous silicon in varying amounts, and this could explain the observed tunability of the PL.

Three good reasons exist to explain why *a*-Si:H mechanism suggested is unlikely. The first reason is that it has been shown<sup>[43]</sup> that as-anodised porous silicon contains little amorphous silicon, the early reports of the amorphous phase were caused by the sample preparation technique causing the amorphisation of the crystalline silicon. Secondly, the PL of *a*-Si:H is known<sup>[48]</sup> to be strongly quenched with increasing temperature from cryogenic temperatures and is clearly not the case for porous silicon which luminesces strongly at room temperature. Finally heat treatment<sup>[15]</sup> on the luminescing material militate against an *a*-Si:H PL mechanism. Raman spectroscopy shows<sup>[15]</sup> that the amorphisation of crystalline porous silicon takes place at around 400°C. It is therefore reasonable to assume the PL intensity would be highest at this point. Instead the PL is quenched at this temperature. Studies<sup>[17]</sup> have also been completed on stain-etched porous silicon from nitrogen-annealed amorphous silicon. These studies show that the porous silicon only luminesces in samples that have been annealed at temperatures in excess of 725°C, and coincide with the emergence of crystalline silicon within the amorphous silicon. It seems more reasonable, therefore, to suppose that the PL comes from either the crystalline silicon, or the interface between the crystalline silicon and amorphous silicon, and not the amorphous phase.

### A.2.1.3 Surface states.

The suggestion that the PL of the 'red' band originates from centres located at the surface of the silicon branches is logical when one considers that the large surface area of porous silicon would provide numerous recombination centres<sup>[48]</sup>. The surface state PL mechanism assumes that absorption of the carriers occurs in the silicon crystallites through a quantum confinement effect<sup>[46]</sup>. The recombination centres are formed by silicon atoms at the surface of the crystallite adjusting their bond lengths and angles to accommodate changes in local conditions. This adjustment of the surface would cause localised changes of the wavefunction that would provide a number of traps at energies lower than the enlarged band gap, explaining the difference between excitation and emission energies. Carriers trapped in these states can then radiatively recombine by a tunnelling mechanism, probably due to the confinement of the carriers in real space. The trapping of both carriers in localised states would cause the decay of the PL to be both relatively long and non-exponential. Changes in the pore environment can be explained by an alteration of the surface states as the atoms again adjusted to suit the change in local conditions.

In highly oxidised porous silicon, where the silicon crystallites are separated from the surface by an oxide layer, it is assumed that the recombination centres occur at the silicon/porous silicon interface. TEM studies have shown, however, that though some silicon crystals display nanometre scale defects, the majority of crystallites are regular and display prominent {111} facets. Thus intense PL could not be expected from such a material which is not the case. Resonantly excited PL also suggests a different PL mechanism to the surface state theory. Using this type of PL it has been shown that excitons couple to momentum conserving phonons whose momentum corresponds to the conduction band minimum of crystalline silicon. This means that the wavefunction is spread over several silicon atoms, and not localised, as is the case of the surface state model.

### A.2.1.4 Quantum confinement.

The quantum confinement model<sup>[2]</sup> for 'red' band light emission was first suggested at the same time that room temperature PL from porous silicon was demonstrated. Here it was argued that the PL was a result of quantum confinement within the nanometre size silicon branches of the porous silicon. This confinement in real space would, under Heisenberg's uncertainty principle, cause sufficient spreading of the wavefunction in momentum space for direct band to band recombination to occur<sup>[44]</sup>. The requirement of nanometre branch dimensions for PL from porous silicon has since been demonstrated<sup>[14]</sup>, together with an observed blue shift with decreasing crystal size<sup>[2]</sup>. Under the quantum confinement model this is also to be expected because reducing crystal size would cause a further widening of the bandgap. The observed temperature dependence of the PL is also explained<sup>[20]</sup> by the band-gap energy shift of silicon with temperature and the thermal broadening is associated with the increase in thermal energy. The observed shorter decay times with shorter wavelength can also be attributed to differing crystal sizes<sup>[20]</sup>; decreasing the size of a silicon crystal increases the overlap between the electron and hole wavefunctions thus decreasing radiative lifetimes.

The most conclusive evidence for quantum confinement induced PL is found using resonantly excited PL<sup>[48]</sup>. These PL spectrums show discrete steps at low temperature which coincide with the zone-edge phonons of crystalline silicon that are known to be involved in the bandgap absorption and emission in crystalline silicon<sup>[22]</sup>. This suggests that the luminescence occurs at the silicon crystallite bandgap. Theoretical calculations and bandgap measurements from transmission studies also concur with this belief<sup>[48]</sup>.

Proponents of the surface state model often attack the quantum confinement model using the observed surface effects, such as the quenching of the PL with either temperature, or the shift in peak intensity with differing oxygen/hydrogen surface passivation. The observed quenching with temperature is easily explained; the number of non-radiative centres, such as dangling bonds, increases with increasing temperature thereby reducing the intensity of the PL<sup>[20]</sup>. The effects of surface passivation are not so easily explained, and it is acknowledged that some modification of the 'pure' quantum confinement model is required in order to account for all observations<sup>[48]</sup>. One such modification has recently been suggested<sup>[45]</sup> and is based on a quantum confinement model where, because of the size of the silicon crystallites, the electronic states are modified by the surface potential. Using a two dimensional model for the overlapping surface chemical bonds, a new set of quantum confined states was obtained which could explain the observed changes with different passivation regimes.

### A.2.2 The 'infrared' PL band

The 'infrared' PL band has generated the least interest amongst researchers and there is a general consensus that the PL for this band originates from radiative dangling bonds on the surface of the silicon branches<sup>[46]</sup>. The main evidence<sup>[37]</sup> to support this theory is that the peak intensity of the PL in this band is seen to occur after annealing a sample in a ultra high vacuum at 350°C. At this temperature hydrogen is known to fully desorb from the surface of the silicon branches which, it is theorised, leaves numerous radiative dangling bonds. The alternative suggestion<sup>[47]</sup> for this PL is that the PL is bandgap or near bandgap PL. This is unlikely because of the intensity and spectral band width of the PL band<sup>[37]</sup>.

### A.2.3 The 'blue' PL band

Two main theories now exist for 'blue' band PL. The first, quantum confinement (described in section A.2.1.4), has been suggested as one possible source of 'blue' band PL. Calculations<sup>[36]</sup> to determine the bandgap of the fine silicon crystallites that exist in most 'blue' band PL-emitting oxidised porous silicon (<2nm) correspond well to the emitted wavelengths of the 'blue' band PL. Oxidised porous silicon does, however, exhibit 'blue' band PL in oxidised porous silicon that shows no discernible silicon crystal structure<sup>[48]</sup>. This implies that even if silicon crystallites did still remain within the oxidised material, efficient 'blue' band PL would be expected only at shorter wavelengths than those observed.

The second suggested mechanism for the 'blue' band PL is that it is an oxide related mechanism<sup>[48]</sup>, either from the oxide itself or from defects<sup>[6,25,36]</sup> or contamination<sup>[34]</sup> within the oxide. FTIR studies have shown<sup>[36]</sup> a correlation between the presence of Si-O-Si bridges in porous silicon and the existence of the 'blue' band PL. For light-assisted anodised porous silicon, which leads to the accumulation of oxygen on the branch surface<sup>[36]</sup>, only a small number of these bridges<sup>[36]</sup> exist, but the PL is also weak. The likelihood of the PL coming from the oxide itself is remote, despite silicon dioxide itself luminescing under appropriate conditions<sup>[49]</sup>. The excitation energy required to excite the

PL in silicon dioxide is much larger than the 3.5 - 4eV used to excite the PL in porous silicon. The PL could, however, result from a non-stoichiometric suboxide,  $\text{SiO}_x$  ( $x < 2$ ), which has a bandgap smaller than that of silicon dioxide<sup>[36]</sup>. For  $x \approx 1.4 - 1.6$  the bandgap of the suboxide is approximately 3 - 4eV, values similar to the excitation energy of the PL in porous silicon. FTIR spectra show, however, that oxide in 'blue' band emitting porous silicon is nearly stoichiometric ( $x < 1.8$ ), making this suggestion unlikely.

The explanation that 'blue' band PL originates from either defects, such as a non-bridging oxygen hole centre, or from contamination of the oxide is more attractive. Having such a near-surface PL mechanism would allow the luminescent regions to be easily modified in the presence of methanol<sup>[25]</sup>. This could not be explained in a quantum confinement model where the silicon crystallites are some distance from the branch surface.

To justify a defect related mechanism the demonstration of blue PL with nanosecond decay from high-purity wet synthetic silica excited by 4eV light is cited<sup>[50]</sup>. The contamination related theory comes from the observed time evolution of the 'blue' band PL<sup>[6,34]</sup>. It is suggested<sup>[34]</sup> that the contamination is carbon related, and originates from both the air and, more specifically, the outgassing of containers in which the porous silicon is stored. Studies<sup>[51]</sup> have been conducted on porous silicon oxidised by RTO and stored in a polystyrene box, a Fluoroware<sup>®</sup> container or a glass dish. PL measurements taken after either 35 days or an artificial ageing process show that 'blue' band PL is obtained from samples stored in either of the first two containers, but not the glass dish. PL measurements of the polystyrene and Fluoroware<sup>®</sup> containers show that this PL has similar properties to that of the oxidised porous silicon, suggesting the same PL source.

It is believed that the contamination is carbon related because comparisons between the stored and artificially aged porous silicon show the PL intensity and carbon concentration of artificially aged material to be approximately twice that of the stored porous silicon. FTIR spectra show the presence of  $\text{CH}_2$  and  $\text{CH}_3$  vibrations in 'blue' band emitting porous silicon. When the sample is subsequently annealed to quench the PL, these  $\text{CH}_2$  and  $\text{CH}_3$  vibrations are no longer evident again suggesting the PL has a carbon related source.

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