Investigation into the Mechanism of Electroluminescence of Porous Silicon in Aqueous Solutions

D.J. Blackwood and A.S.L. Chong
Department of Materials Science
National University of Singapore
Lower Kent Ridge Road, Singapore 119260

Since the advent of visible room-temperature luminescence from porous silicon in 1990,(1) extensive works by many groups have been carried out in trying to pinpoint the source or sources of the luminescence, with models based on quantum confinement affects, absorbed surface species and surface states being proposed.(2-4) In the present work the electroluminescence spectrum emitted from n-type porous silicon polarised in a solution of sodium persulphate was followed in real time. This revealed that the spectrum evolved through several changes during the first few tens of seconds after the onset of electroluminescence.

Specimens were cut from 6-inch (100)-orientated n-type silicon wafers with resistivities between 1-5 Ω cm. Gallium-Indium eutectic was used to make ohmic contacts to the backside of the wafers. The porous silicon was obtained by electrochemical etching in a solution of 1:1:2 HF:H_2O:ethanol held in a two-electrode PTFE closed-cell under the illumination of a xenon halogen lamp for 10 minutes. The electroluminescence experiments were conducted in a three compartment glass electrochemical cell containing 0.1 M $K_2S_2O_8$ + 1 M H_2SO_4. A constant potential was then applied and the evolution of the resultant electroluminescence spectra was recorded via a MS257™ Spectrograph with an Andor CCD detector (Oriel DV420-Bu).

Figure 1 shows a typical sequence of electroluminescence spectra. Initially weak electroluminescence was observed with maximum intensity at a wavelength of 720 nm (Peak A). Within about five seconds the intensity of the electroluminescence increased approximately by a factor of six and the peak wavelength shifted to 620 nm (Peak B). However, after about 20 seconds the intensity was observed to decrease whilst the maximum underwent a gradual red-shifting to 670 nm (Peak C). Finally, between 40 and 100 seconds the maximum again blue-shifted to 630 nm (Peak D) where it remained until the end of the 300 seconds experiment, although the intensity continued to gradually decrease.

The pattern of blue-shifting (A→B), red-shifting (B→C) and finally blue-shifting again (C→D) was found to occur whenever the porous silicon was polarised at any potential between -1900 mV and –1650 mV. However, at potentials positive to -1600 mV Peak A was no longer observed, whilst positive of –1500 mV Peak B was also not present. In addition the wavelengths at which the various peak intensities occurred were observed to vary with the polarisation potential as shown in Table 1. Occasionally the electroluminescence spectrum resolved into a doublet. This indicates that several different processes contributed to the luminescence and that the shifts in the intensity maximum probably resulted from variations in the relatively rates of these processes.

Although at present there is insufficient data to fully assign the four peaks, it is thought that the final weak Peak D is due to the quantum confinement of the nanosized silicon with the other three peaks being due to surface species or states. Peaks A and B only appeared at certain potentials, which suggests these are related to adsorbed species, whilst Peak C was the least affected by the applied potential, so it is probably not associated with a surface states associated with imperfections of the nanocrystals. Alternatively, Peak C may be due to the silicon nanocrystallites themselves with the blue shifting to Peak D being caused by oxidation processes leading to a reduction in the size of the crystallite cores.

The most likely surface species responsible for the weak Peak A is some form of SiH_x, which has been identified on the surface of fresh porous silicon by FTIR. Ohmukai et al(5) have claimed these silicon hydride species photoluminesce at 730 nm, very close to the maximum of Peak A at 720 nm. If SiH_x present, it is highly possible that when the applied bias was switched on, this species oxidised rapidly to oxyhydrides, and hence the electroluminescence peak associated with it disappeared after a few seconds. However, it is not yet known whether these oxyhydrides could be responsible for the strong luminescence of Peak B.

References:
1. L. Canham, *Appl Phys Lett.* **57** (1990) 1046.
2. C. Delerue, M. Lannoo, G. Allan, *J. Lumin.*, **57** (1993) 249.
3. S.M. Prokes, *J. Appl. Phys.*, **73** (1993) 407.
4. V. Lehmann and U. Gosele; *Appl. Phys. Lett.* **58** (1991) 856.
5. M. Ohmukai, A. Kobayashi and N. Uehara *"Luminescent Materials"*, p. 163 (Proceedings of MRS Spring Meeting, San Francisco, 1999).

Table 1. Dependence of electroluminescence peak positions on applied potential.

Peak maximum (nm)	**A**	**B**	**C**	**D**
-1900 mV	720	620	670	630
-1700 mV	770	640	695	650
-1650 mV	800	680	675	625
-1600 mV	-	675	685	650
-1550 mV	-	640	700	670
-1500 mV	-	-	674	610
-1350 mV	-	-	700	628

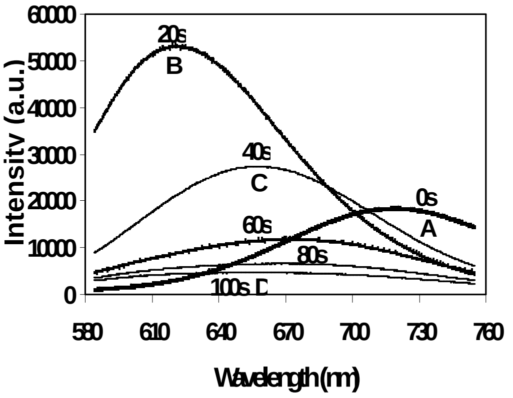

Figure 1. Evolution of the electroluminescence spectra of n-type porous silicon held at -1900mV in 0.1M $K_2S_2O_8$ + 1M H_2SO_4.