## LUMINESCENCE IN POROUS SILICON

# Voltage Control of the Colour

Recent results reported by a group* from Grenoble showing that luminescence in porous silicon with wet internal contacts can be adjusted by varying the applied voltage may soon be extended to systems with solid internal contacts.

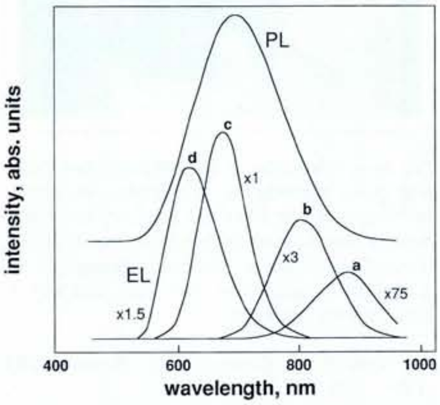

*Fig. 1 — Photoluminescence (open-circuit conditions) and electroluminescence spectra of porous silicon obtained in 0.2 M solution of* $(NH_4)_2S_2O_8$ *for a cathodic bias of -1.0 V (a), -1.2 V (b), -1.5 V (c), and -1.6 V (d).*

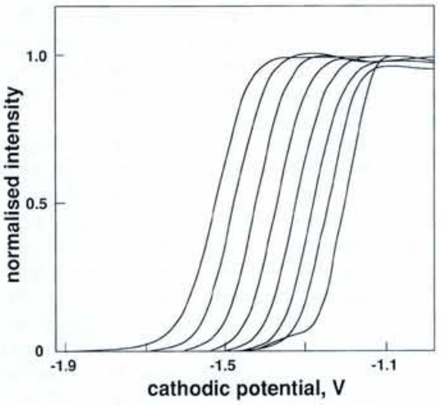

*Fig. 2 — Photoluminescence intensity as a function of the applied cathodic voltage for various luminescence energies (from left to right: 2.00 eV, 1.88 eV, 1.77 eV, 1.68 eV, 1.59 eV, 1.51 eV, 1.44 eV, 1.35 eV).*

The electroluminescence of semiconductors has received much attention and is currently used in devices such as laser-emitting diodes. But several handicaps prevent a wider application, among them the low efficiency of bulk silicon and the difficulty semiconductors have in exhibiting emission tunable over a wide wavelength range comparable to those for dyes or for transition metals ions in insulators, for example. The situation may soon change owing to some recent observations made on porous silicon.

Porous silicon [see *EN* **23** (1992) 183] with its important surface/volume ratio offers a large surface area accessible to electrochemical liquids used for carrier injection or the application of electric fields within the material. This brief report describes how the electroluminescence (EL) and photoluminescence (PL) of porous layers electrochemically etched in n-type substrates can be manipulated by applying these conditions

### Voltage-Tuned Electroluminescence

With electrochemical injection, a perfectly reversible and stable EL is obtained which shows an interesting dependence of the wavelength and intensity on the cathodic polarization and on the texture of the porous layer. The position of the peak in the EL spectrum is found to be a linear function of the applied voltage (Fig. 1) while its intensity mainly depends on the injected current; varying the electrolyte concentration allows one to change these two parameters independently. The texture of the porous silicon, which can be modified by the illumination conditions during film formation, affects both the PL and EL, but in each case the envelope of the EL spectra obtained at various voltages coincides with the PL spectrum.

EL arising from a voltage-selective electroexcitation of an inhomogeneously broadened optical transition is able to explain most of the observations. Assuming the porous silicon contains an array of quantum dots, the possibility of a selective excitation of a given subset of the dots which contributes to the optical line shape and thereby induces fluorescence line narrowing is unsurprising when the excitation is obtained by a laser excitation [1]. However, it is original when the selectivity is provided by the electro-injection of carriers at energies determined by the applied voltage [2]. The model takes into account the simultaneous injection selectivity of majority carriers which come from the substrate as well as those of the minority carriers resulting from the redox reaction in the electrolyte. This double selectivity explains why it is possible to tune the EL spectrum by varying the applied voltage.

### Voltage-Selective Quenching

The inhomogeneous distribution of the sizes of the quantum dots that gives rise to the inhomogeneous broadening of the optical transition can also be invoked for the voltage-selective quenching of the PL, which has been observed for n-type porous silicon under polarization in an aqueous solution [3]. Starting at low voltages, a luminescence quenching on the red side of the PL spectrum shifts continuously to the blue side with increasing cathodic voltage until a total quenching is obtained (Fig. 2). Here again, the photon energy at the onset of quenching is a linear function of the applied potential. Using time-resolved PL measurements it has been verified that the quenching is not due to an acceleration of the non-radiative processes. These observations contrast with what has been observed [4] when the field is applied using solid contacts; in this case a quenching is indeed observed, but at a much higher voltage and without a voltage-selective effect.

A model closely related to the previous one is proposed. It also uses the idea of a voltage-selective feeding of quantum dots but only the majority carriers have to be taken into account since the redox species in the electrolyte are absent. If one supposes that this feeding is efficient enough to accumulate carriers in the dots whose confined levels match the energies of the majority carrier, light-induced carrier injection will be prevented thus giving rise to the PL quenching.

It is interesting to note that the idea of selective carrier injection was first developed by Lehmann *et al.* [5] while considering very different phenomenon associated with the electrochemistry of porous silicon. In our case, the only unverified assumption which remains is the effect of carrier accumulation on the absorption coefficient. Preliminary optical saturation measurements indicate that saturation can be obtained for an optical flux which roughly corresponds to one photon (and therefore to a single electron-hole pair) per quantum dot. It is therefore believed that the hypothesis of selective carrier injection is realistic.

Porous silicon has inspired so much interest among semiconductor physicists that is is unlikely that the observations obtained with wet internal contacts will not be reproduced with solid internal contacts. Indeed, the improvement in solid-contacted electroluminescence by metallic electroplating and by filling of the pores with polymers which was recently reported [6] confirms this assumption.

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[2] Bsiesy A. *et al., Phys. Rev. Lett.* **71** (1993) 637.
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[5] Lehmann V. & Gösele U., *Appl. Phys. Lett.* **58** (1990) 856.
[6] *Luminescence of Porous Silicon & Silicon Nanostructures* (Les Houches School, 7-12 February 1994).

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