Voltage-Controlled Spectral Shift of Porous Silicon Electroluminescence

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In this paper, it is reported that the electroluminescence (EL) of porous silicon shows a reversible spectral shift as large as 270 nm for an external bias variation of 0.6 V. This electroluminescence is obtained upon cathodic polarization of lightly doped *n*-type porous silicon in contact with aqueous persulphate solutions. The study of the EL behavior as a function of the external voltage and the persulphate ion concentration proves that while the amplitude of the EL is proportional to the intensity of the exchanged current, the spectral position is only determined by the applied voltage.

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Visible photoluminescence (PL) observed on highly porous silicon layers obtained by electrochemical etching of crystalline substrates has recently been reported [1,2]. This surprising optical property of silicon has been attributed to the fact that the porous layer is formed of quantum-size entities where a confinement effect takes place provoking the observed visible photoluminescence [1-3]. Selective excitation of the PL has shown that the observed emission is inhomogeneous [2,4]. It has been proposed that the corresponding wide line shape is due to the size distribution of the quantum-size crystallites which results in a wide confinement energy distribution.

Bright visible light emission can also be obtained by electrical excitation during anodic oxidation of highly porous *p*-type silicon layers in contact with aqueous solutions [5]. It results from radiative recombination between the holes supplied by the bulk of the *p*-type semiconductor and the electrons injected from the electrolyte or from the crystallite surface. It has been proposed that the oxidation of the Si-H bonds which initially cover the porous silicon surface [6] might be responsible for the electronic injection [5]. However, such electroluminescence (EL) is accompanied by a rapid and irreversible modification of the porous material through its partial oxidation which finally results in the quenching of the electrical excitation [7].

A similar electroluminescence has been observed on a cathodically polarized *n*-type porous silicon in contact with $S_2O_8{}^{-2}$ (persulphate) concentrated solutions [8,9]. The reduction of the $S_2O_8{}^{-2}$ ion leads to a very reactive intermediate oxidant $SO_4^{\bullet -}$ [10] whose reduction results in hole injection into the crystallite where a radiative recombination takes place with the electrons supplied by the cathodically biased substrate. This light emitting junction is very attractive because in this case the oxidation of the material, and consequently its evolution, are almost totally avoided. This rather stable and very efficient light emitting system might also bring some improvements in our understanding of the luminescence properties of porous silicon.

Porous silicon is formed by anodization of *n*-type (100) silicon samples (8×10^{14} cm^{-3}) in HF aqueous solution using a classical experimental setup. The electrolyte is composed of two parts de-ionized water, five parts ethanol, and three parts HF 50%. The anodization is performed under illumination with a tungsten lamp in order to get the hole ($h+$) supply required for silicon etching. The lamp power, current density, and anodization time were 40 mW/cm^2, 5 mA/cm^2, and 10 min, respectively. The resulting layer is 2 μm thick with a porosity of about 80%. In these conditions, no macroporous structure is obtained [11].

Cathodic polarization was scanned between -0.4 and -1.8 V versus a saturated calomel electrode (SCE) at 25 mV/s in freshly prepared $1M\,H_2SO_4$ aqueous solutions containing various $(NH_4)_2S_2O_8$ concentrations (0.05, 0.1, or 0.2*M*). A forward ($-0.4\rightarrow-1.8$ V) and a reverse scan ($-1.8\rightarrow-0.4$ V) formed a single run. The resulting current intensity was measured using an electrometer and the emitted EL spectra was recorded and analyzed using an optical multichannel analyzer coupled to a cooled charge-coupled-device array detector.

The current-potential (*I-V*) curve obtained in 0.2*M* $(NH_4)_2S_2O_8$ solution is shown in Fig. 1(a). The $S_2O_8{}^{-2}$ reduction current appears for a polarization lower than -0.8 V which corresponds roughly to the flat-band po-

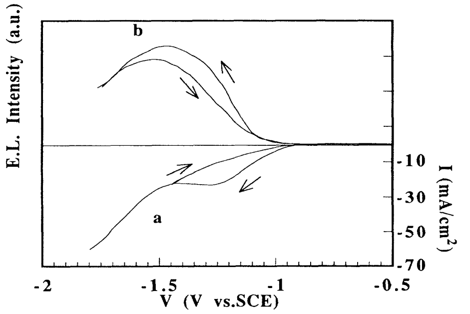

FIG. 1. Cathodic current (a) and λ-integrated EL (b) obtained for 0.2*M* $(NH_4)_2S_2O_8$ as a function of the cathodic bias. The forward and the reverse scans are represented.

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tential of *n*-type Si in an aqueous solution [12]. For a potential around -1.2 V a current shoulder is observed which is found to be proportional to the $S_2O_8{}^{-2}$ ion concentration. For potentials more negative than -1.3 V the current increases rapidly as a result of the H^+ reduction which takes place by an electronic exchange with the conduction band. This reduction results in an intense hydrogen bubbling which can perturb the luminescence detection and therefore the cathodic bias cannot be further increased. We have thus chosen to stop at -1.8 V. The corresponding λ-integrated EL intensity is recorded as a function of the cathodic polarization [Fig. 1(b)]. The EL signal appears at -0.9 V and the intensity increases rapidly, passes through a maximum (EL-max), and then decreases continuously. During the reverse scan, the current is found to be smaller than that observed for the forward scan while the EL starts to increase again and shows a second maximum which is obtained for nearly the same bias as the first EL-max. The same behavior is obtained whatever the $S_2O_8{}^{-2}$ ion concentration, and EL-max is found to be proportional to the ion concentration in the studied range.

The evolution of the current clearly indicates the depletion of the oxidizing agent at the electrode surface which should indeed take place in our conditions where a stationary electrode is used. This would well account for the first EL-max; the depletion of the oxidizing agent results in a decrease of the hole exchange current leading to a decrease in the EL intensity. However, during the reverse scan, the EL intensity shows another EL-max whereas the reactive species depletion would have induced a continuous decrease of the emitted light during this scan. This behavior proves that the observed reversible EL modification is not related to a concentration effect but must be governed by the external voltage. On the contrary, the fact that the second EL-max is found to be of a smaller value is an oxidant depletion effect. A possible explanation of this bias-induced EL modification will be discussed in the following part.

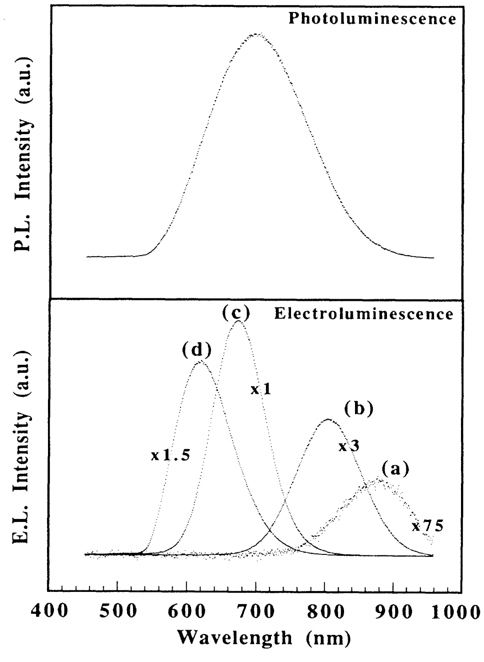

FIG. 2. PL (open circuit conditions) and EL spectra obtained in $0.2M$ $(NH_4)_2S_2O_8$ for different cathodic bias: (a) -1 V, (b) -1.2 V, (c) -1.5 V, and (d) -1.6 V.

The EL spectra show a large reversible shift upon cathodic biasing. Figure 2 presents several spectra recorded at different voltages during a typical scan. A quite important peak shift, from 880 nm at -1 V to 610 nm at -1.6 V, is observed. This emitted light, whose color is seen to change from dark red to bright green as the voltage is increased, is easily visible to the naked eye even in daylight. The peak energy is nearly proportional to the external voltage with a slope equal to 1 as illustrated in Fig. 3. On the other hand, the FWHM of the EL is found to be much narrower (0.25 eV) than that of the PL signal (0.6 eV). Furthermore, the observed PL can be considered to be roughly the envelope of all the emitted EL spectra as shown by Fig. 2. This strongly suggests that in this case we are in the presence of a selective excitation of the porous silicon luminescence, which has been found, as already mentioned, to be inhomogeneous [2,4]. This selective excitation is induced by the cathodic bias. This spectral tunability could be compared to that obtained in the case of a semiconductor laser where the inhomogeneous luminescence of a multiquantum well InGaAs/InP structure has been used to scan the laser wavelength of about 200 nm in the infrared range (1440–1640 nm) [13]. In this case, the tunability is obtained by modifying the external-cavity configuration.

In order to better understand the origin of the spectral shift as well as the EL behavior one must examine the charge exchange mechanism at the porous Si-electrolyte interface. The highly porous silicon is formed of quantum-size crystallites of different dimensions in which a quantum confinement effect takes place. A large distri-

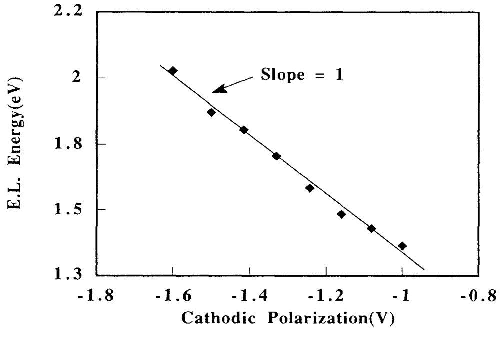

FIG. 3. Emitted photon energy as a function of the applied voltage for a cathodically biased *n*-type porous silicon layer.

bution of the confinement energy results from this size distribution which can be represented by a Gaussian law. In the same way, the electroactive species is characterized by an energy distribution related to the fluctuation of the solvatation. A typical value of the FWHM of such a distribution is 1 eV in an aqueous solution. Because no EL is observed when no electroactive species is present, it is likely that the EL observed in the cathodic range is governed by the hole exchange current between the electrolyte and the different crystallites. This current is determined by the product of the hole confinement energy distribution and the $SO_4^{\bullet}$ energy distribution shown in Fig. 4. It depends on the cathodic polarization and can lead for a certain bias to a maximum in the h^+ injection current when the distribution maximums match. For this given bias, the emitted EL should be maximum which is in agreement with the experimental results reported above.

This mechanism can also explain the observed spectral shift. The injection of holes with increasing energy allows progressively the charge exchange with smaller crystallites. A bias-induced blue shift is then expected, in agreement with the experimental results. In addition, one must note that the spectral position of the EL is determined by the cathodic bias but could be also affected by the value of the exchanged current as proposed by Canham [9]. In order to check the dominant phenomenon, variations in the cathodic current, independently of the voltage, were obtained by changing the concentration of the electroactive species. Figure 5 shows that when the $S_2O_8^{-2}$ concentration is doubled, the cathodic current is increased, but no differences are obtained in the potential dependence of the wavelength peak.

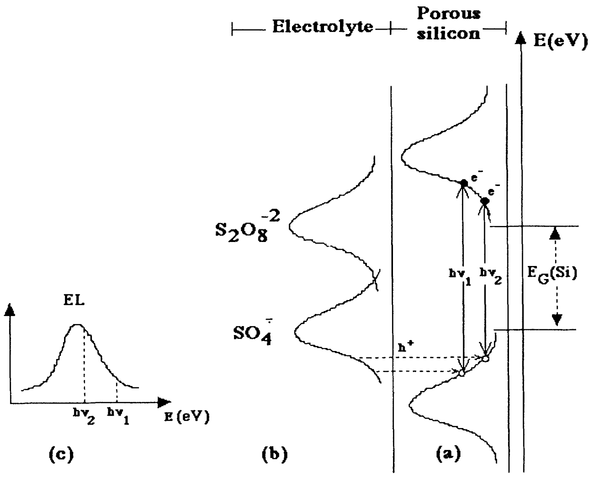

FIG. 4. Energy band diagram showing (a) electron and hole energies and their distribution in the porous silicon and (b) redox species ($S_2O_8^{-2}$ and $SO_4^{\bullet}$) solvatation energy distribution [same energy scale for (a) and (b)]. Scheme (c) represents the product of the energy distribution of holes by the solvatation energy distribution of $SO_4^{\bullet}$ which gives the EL spectrum. This product is shifted by the applied voltage.

Assuming that no voltage drop occurs in the bulk of both the silicon and the electrolyte (as is the case for a metal or a semiconductor in conditions of charge accumulation), a variation ΔV in the applied voltage will induce an energy shift $\Delta E_h = e\Delta V$ of the distribution maximum of the selected holes. Since for a given crystallite the electron and hole confinement energy (E_e, E_h) are roughly equal [14], the shift of the luminescence energy $h\nu = E_G + E_h + E_e$ is expected to be $\Delta h\nu = 2e\Delta V$. The experimental results (Fig. 3) give a factor equal to 1 which might show that in our case the applied polarization is not totally found at the porous Si-electrolyte interface but must be shared with the porous silicon bulk. In fact one should also take into account the finite distribution width of the electroactive species and the crystallite energy levels whose product gives the photon energy distribution. Simple mathematical arguments show then that the maximum of this distribution is shifted by a smaller factor.

This qualitative model seems to be able to explain the major characteristics of the cathodic EL. Nevertheless, some difficulties are still to be overcome. For instance, the proposed model does not in its present state explain the surprisingly narrow EL spectrum. In fact, the two mentioned energy distributions have roughly the same width (0.6–1 eV) in such a way that the resulting product is expected to be of the same order of magnitude rather than the observed 0.25 eV. We think that this point may be clarified by considering other possible limiting mechanisms such as the injection of the majority carriers. This carrier supply, provided by the cathodically biased substrate, must be enhanced by the increasing voltage which tends to reduce the energy difference which initially exists between the bulk of the material and the confined levels of the quantum-size crystallites. Such kind of investigations are at present conducted in our laboratory.

The EL signal observed upon cathodic polarization of n-type porous silicon has been studied in detail in this paper. A selective excitation of the inhomogeneous luminescence of the porous silicon seems to take place in these

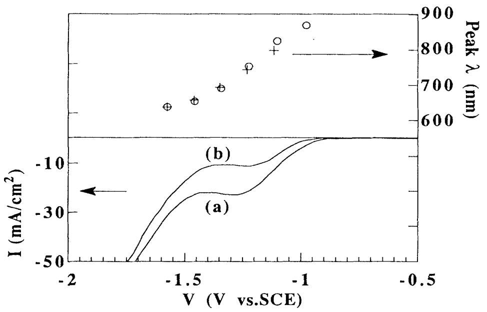

FIG. 5. Cathodic current and EL peak wavelength obtained for 0.2M (a,○) and 0.1M (b,+) $(NH_4)_2S_2O_8$ as a function of the cathodic bias.

conditions. Experimental evidence for a large range of voltage-tunable EL spectra has been presented. To our knowledge, the porous silicon is the only semiconductor where such an interesting property is evidenced. A similar voltage-tunable EL spectra obtained with a solid phase contact would surely lead to many interesting applications.

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