Morphological changes in porous silicon nanostructures: non-conventional photoluminescence shifts and correlation with optical absorption

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Abstract

In this paper, we show that the photoluminescence (PL) shifts of p-type porous silicon (PS) are mainly attributed to some morphological changes related to anodisation conditions. We discuss how differences in the stirring and nature of the electrolytic solution can lead to morphological changes of the PS layers. It has been found that when PS is formed in pure aqueous HF solution, it can exhibit a non-conventional and reproducible porosity PL peak relationship. By correlating the PL spectral behaviour and PS morphology throughout a quantum-confinement model, we explain both conventional and non-conventional PL shifts. Correlation of PL and optical absorption (OA) shows that the PL peak energy and the optical absorption edge of PS exhibit the same trend with size effect. The spectral behaviour of OA with regard to that of PL is well analysed within the quantum-confinement model throughout the sizes and shapes of the nanocrystallites forming PS. The value of the effective band gap energy determined from the calculated lowest PL energy almost corresponds to that estimated from the optical absorption coefficient. These results suggest that the lowest radiative transition between the valence band and the conduction band corresponds to the largest luminescent wires, and that the radiative recombination process leading to the PL emission occurs in the c-Si crystallite core. © 2000 Elsevier Science B.V. All rights reserved.

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Keywords: Photoluminescence; Porous silicon; Nanostructures; Absorption

1. Introduction

While p\textsuperscript{+}-type PS has crystallites almost in the form of wire \cite{1,2}, the structure of p-type PS is rather complex and often represented by
undulating wires [1]. Although different structures have been suggested to describe the morphology of p-type PS [1,3–5], a quantitative correlation of its optical properties with its morphological aspects is not well established yet. One of the major problems is the complexity of the structure of the material which is mainly due to the scarcity of uniformity in the shape and size of the crystallites and to the variety of preparation conditions. This correlation could contribute to the understanding of the optical properties of PS. There is now a general consensus that the radiative transitions leading to visible PL arise from confined states in the c-Si crystallite core [6,7]. Despite these arguments, it is sometimes hazardous to consider only the pure quantum effects when interpreting shifts of the luminescence spectrum, without considering the effects of preparation parameters on both morphology and optical behaviour of PS. As far as we know, attempts to correlate PL and OA taking into account the structural and morphological aspects of PS are still lacking.

In this paper, we try to review this question by demonstrating that some non-conventional observations (apparently in contradiction with quantum size effects) may be explained within the quantum-confinement model (QCM) when all morphological aspects and relevant factors have been taken into account. We show that the spectral behaviours of the OA are well interpreted within the QCM. Band gap calculation using theoretical PL spectra described within the QCM fit entirely the experimental values.

2. Experimental

The PS layers are obtained by anodisation of (1 0 0) oriented boron-doped silicon substrates of 1-1.5 $\Omega\cdotcm$ resistivity in stirred aqueous and ethanoic HF solutions, at constant current densities for various periods. Aqueous and ethanoic HF solutions are prepared from 49% HF by adding deionised water and pure ethanol, respectively. After anodisation the PS layers are rinsed in deionised water and dried in ambient under nitrogen flux, the samples are then stored in a dry dark box in order to preserve the characteristics of fresh PS layers. The porosity and thickness of the PS layers are determined by the gravimetric method; to approach the real porosity values, triplicate measurements are made. In order to pull off the PS layer from the substrate and to obtain homogeneous free-standing membranes suitable for optical transmission measurements, the current density was raised up to 500–1000 mA/cm$^2$ (depending on the thickness of the layer) for 2 s, at the end of the electrochemical process. The PL spectra was monitored using a set-up consisting of a triple grating spectrometer, a GaAs photomultiplier and the 5145 Å line of a 10 mW Ar$^+$ laser. Optical transmission was measured using a Jobin Yvon spectrophotometer equipped with an integrating sphere. All spectroscopic data were measured at room temperature. The specific features of realised PS samples are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of aqueous HF solution (%)</th>
<th>Concentration of ethanoic HF solution (%)</th>
<th>Current density (mA/cm$^2$)</th>
<th>Anodisation time (mn)</th>
<th>Porosity (%)</th>
<th>Thickness (µm)</th>
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<tr>
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<td>3</td>
<td>–</td>
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<td>–</td>
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<tr>
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<td>10</td>
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Table 1
Specific features of studied PS layers
3. Results and discussions

3.1. Effect of forming conditions on PS morphology

In this part, we try to recall the specific features of the PS layer prepared in ethanoic and aqueous HF, although they have been roughly discussed in the literature. The dependence of these features with anodisation conditions seems to be determinant to correlate the PS structure with its PL properties.

Fig. 1 depicts the variation of the thickness of the PS layer as a function of anodisation time. For PS prepared in ethanoic HF, the variation of the thickness of the PS layer versus anodisation time is quite linear (Fig. 1a) in the range of 5–25 mn. However, this variation is not linear for very short anodisation times, due to the fractal character and the complexity of the nucleation of the porous structure. The porosity (65%) of the PS samples is almost constant and independent of anodisation time (cf. Table 1); these results are in good agreement with those obtained in other works [8,9] and would suggest, as always reported, that anodisation in ethanoic HF solution is homogeneous.

In contrast, in aqueous HF solution, the variation of the layer thickness with anodisation time is not quite linear (Fig. 1b). This might be due to morphology variation as the PS layer becomes thicker. The increase of the porosity (cf. Table 1) with anodisation time is reproducible and would result from morphological variations. In this case, the PL behaviour resulting from the variation of anodisation time or current density is a complex piece of information (cf. Fig. 3). Before interpreting the non-conventional PL behaviour of PS formed in aqueous HF, we must first understand what happens in the whole structure of the PS layer and why morphology would change during anodisation.

One can notice (Fig. 1) that for the same anodisation time, the PS layer is thicker when prepared in aqueous HF solution than in the ethanoic one. One could also notice a rapid increase of the layer thickness of PS prepared in aqueous HF, when it exceeds 20 µm. We believe that nothing is special about this thickness but would simply indicate that the reaction rate in aqueous HF depends on layer thickness. It is well known that PS formation produces hydrogen bubbles. In ethanoic HF solution, the presence of ethanol improves the wettability of the material by preventing hydrogen bubbles formation. As a result, the ethanoic HF solution completely infiltrates the pores and the layer grows uniformly, whether or not the solution is stirred. To see the influence of stirring and hence hydrogen bubbles (in aqueous HF) on the morphology of the PS layer, we have performed SEM analysis. Fig. 2(a) and (b) shows the effect of stirring on the morphology of a PS layer (A6510) prepared in aqueous HF. One can notice (Fig. 2a) that stirring induces a roughly homogeneous surface, with the presence of few pores having a mean size of ~100 nm. However, when the stirring is suppressed, the surface of the same PS layer (A6510) becomes very disordered with the presence of nodules, protuberances and cracks (Fig. 2b) due to tension forces, thus indicating an electrochemical etching inhomogeneity.

Nevertheless, one may guess that, even in a stirred aqueous HF solution, when the PS layer becomes thick enough (t > 10 mn), the hydrogen bubbles remain more and more in contact with the deep crystallite walls, leading to inhomogeneous etching in the deeper parts of the porous structure. In such a case, the local current density would increase at the regions free of bubbles, essentially near the top surface where hydrogen bubbles are
scarce, as well as at the PS/silicon interface (since hydrogen bubbles formed at the interface tend to go up the pore walls). The increase in the local current density, near the top surface, would be responsible of the loss of material (removal of subsurface crystallites) not associated to Faraday’s law (2 charges per dissolved Si atom) as the PS layer grows. However, the increase in the local current density at the PS/silicon interface would induce an HF concentration gradient [10] favouring high porosity formation. The combination of these two effects may explain the increase of porosity in doubling the anodisation time at constant current density and HF concentration (cf. Table 1).

However, doubling the anodisation time results in a thickness increase (cf. Table 1) less than a factor of 2 (from A6510 to A6520), or more than a factor of 2 (from A8010 to A8020). In fact, as we go toward higher current densities, hydrogen bubbles become more and more present in the whole porous structure, even near the top surface, making the whole process poorly reproducible. Hence, doubling the anodisation time at high current density (from A8010 to A8020) may further increase the local current density at the PS/Si interface (which is free of bubbles) leading to a more important thickness variation than in the case of low current density (from A6510 to A6520). This explanation is in good agreement with the obtained experimental results (cf. Table 1).

Further, it would be interesting to compare the features of two samples prepared under the same conditions, but one in aqueous HF (A6510) and the other in ethanoic HF (E6510) (cf. Table 1). As the hydrogen bubbles are abundant during the formation of the aqueous sample (A6510), they should induce an increase in the local current density and the local porosity at the regions free of bubbles. However, since the neighbouring deep areas are blocked by bubbles, they should remain unattacked. This leads to a lower porosity and a thicker sample (in comparison to the E6510 ethanoic sample), which is in agreement with the experimental results shown in Table 1.

3.2. Interpretation of the PL energy shifts

In this part we study all PL behaviours (redshift or blueshift) induced by the forming conditions of PS. Fig. 3 depicts experimental and theoretically calculated PL spectra, for different anodisation times and current densities; it should be noticed that all data are reproducible for the PS layers (prepared in 20% aqueous HF solution) for which anodisation may be considered as inhomogeneous. Two other PL spectra corresponding to PS prepared in 3% aqueous HF and 20% ethanoic HF are given for comparison purposes. The PL spectra were measured in vacuum after stabilisation of the PL intensity, where no evolution of the PL peak
energy with time was observed [11]. Many different mechanisms have been proposed to explain the PL properties of PS, but the quantum confinement model has presently the most support. TEM studies [1,2] show that there exist cylindrical and spherical crystallite shapes in p-type PS. It is therefore reasonable to consider PS as a mixture of QWs and QDs of different concentrations and sizes. The theoretical PL spectra are thus calculated by using a simple quantum confinement-based model [5,11] where the visible red luminescence is only produced in QWs and QDs. A dependence of $d^{-1.39}$ for the energy gap versus the crystallite diameter, $d$ [12], has been adopted; we also assume that luminescent wires and dots have concentrations $x_w$ and $x_d$, respectively, with a Gaussian distribution of their diameters centred around means $d_{0w}$ and $d_{0d}$. We can notice that for some PS samples (e.g., A6510 and E6510) the theoretical PL spectrum does not fit exactly experimental data at the low PL energy side. This can be explained by the fact that for PL energies below 1.5 eV, surface states contribute to a weak PL emission in the near-infrared region [13,14].

From the fitting of theoretical PL spectra to experimental ones, one can estimate the concentrations $x_w$ and $x_d$, the mean diameter sizes $d_{0w}$ and $d_{0d}$ of QWs and QDs and the root mean square $\sigma_w$ and $\sigma_d$, respectively. Table 2 shows the optimised fitting parameters corresponding to the theoretical PL spectra of Fig. 3.

Fig. 4 shows the theoretical PL spectrum of A6510 PS sample, where both QWs and QDs contribute to the total PL spectrum. One may note that QWs contribute to emission at the low PL energy side while QDs contribute to the PL spectrum at high energies. The PL behaviour (blueshift or redshift) depends on both crystallite size and concentration of QWs and QDs. In other words, a decrease in the crystallite size does not automatically signify a PL blueshift, since size reduction may be accompanied by an appreciable increase in the QWs concentration leading to a PL redshift [5].

Let us analyse the effect of the increase of anodisation time on the PL spectra for different current densities (Fig. 3). One can see, that although giving higher porosities (cf. Table 1), the increase of anodisation time in aqueous HF redshifts the PL peak position in a reproducible way, whatever the current density may be. This behaviour may be considered as non-conventional,

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**Table 2**

Optimised fitting parameters corresponding to the theoretical PL spectra shown in Fig. 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x_w$ (%)</th>
<th>$d_w$ (nm)</th>
<th>$\sigma_w$ (nm)</th>
<th>$x_d$ (%)</th>
<th>$d_d$ (nm)</th>
<th>$\sigma_d$ (nm)</th>
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<td>0.43</td>
<td>5.5</td>
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<tr>
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<td>51</td>
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<td>B8020</td>
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<td>0.3</td>
<td>70</td>
<td>3.3</td>
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Fig. 4. Theoretical PL spectra of sample A6510, showing the contribution of QWs (dashed lines) and QDs (dotted lines) to the total PL spectrum. Calculations are made using the parameters of Table 2.

far from the well-known “porosity–PL peak shift relationship”. One can also notice (Fig. 3) that the increase of the current density has spoiled the effect of anodisation time.

As previously mentioned, up to a certain thickness, hydrogen bubbles are relatively scarce in the deep regions of the PS layer, allowing the electrochemical etching to remain quasi-homogeneous. For relatively long anodisation times ($t \geq 10$ mn), the thickness of the PS layer goes beyond a certain critical value above which anodisation becomes inhomogeneous. At this stage, in the deeper regions of the PS layer (far from the surface) the formed hydrogen bubbles cannot be easily removed, even when the electrolytic solution is well stirred. This prevents etching of the deep structures (undulating wires [5]), which remain relatively large as the PS layer grows. The partial coverage of the deeper parts of the PS layer by hydrogen bubbles should increase the local current density (at the internal surface) in some parts of the layer, especially near the surface where the structure is more opened [1,2] and essentially composed by interconnected dots [4,5], and at the PS/silicon interface (as previously mentioned). This favours the removal of intensely luminescent subsurface small crystallites (free of bubbles) or allow them to attain a certain crystallite size limit at which they cannot be probed with the 5145 Å laser line. Hydrogen bubbles may also break the most fragile and small structures leading to a loss of material; this breaking may occur at the drying stage. If we refer to quantum size effects, this may explain the decrease of the PL intensity and the redshift of the PL peak position of aqueous PS samples when anodisation time increases (i.e., increase in the thickness). This is in good agreement with the calculation results for aqueous PS samples (cf. Table 2), where we notice a preponderance of QWs concentration at the expense of that of QDs and an increase of the crystallite mean diameter sizes, when anodisation time increases.

Long anodisation time under an aggressive regime (e.g., sample A8020), favours further and further hydrogen bubbles formation, which prevent etching not only at the deep part of the PS layer but in the major part of the porous volume. Consequently, the smallest interconnected dots forming the undulating wires [5], as well as the amorphous silicon-covered QDs are firstly disconnected leading to dots rupturing and the preponderance of QWs (cf. Table 2). In fact, when low-current density is applied (sample B8020) in a stirred low-concentration aqueous HF solution, the electrochemical etching process is not aggressive and produces less hydrogen bubbles than in a thin PS layer formed at rather high-current density (Table 1). All these conditions allow to form a less distorted morphology throughout electrochemical etching homogeneity and would explain why PS sample prepared in this manner has a finer structure (Table 2). This may also explain the large PL peak blueshift of B8020 with respect to A8020.

The difference between the PL spectra of A6510 and E6510 (two PS samples prepared in the same anodisation conditions, cf. Table 1) is simply a consequence of electrochemical etching homogeneity and hence would be due to morphology difference.

3.3. Correlation of PL and optical absorption

Transmission is the sole method sensitive to the whole size distribution of PS. Fig. 5 shows the spectral behaviour of the OA of A6510 and A6520 PS samples, with their corresponding PL spectra. Transmission spectra show that the optical
absorption edge (OAE) lies approximately between 1.8 and 2.6 eV. Thus, one may deduce (Fig. 5) that in the OAE spectral range, the PL and the OA coefficient exhibit the same trend with preparation conditions.

The well-known Stokes shift between the laser excitation energy and the PL band implies that the population of the crystallites that absorb are different from those that luminesce. Therefore, the crystallites contributing to the PL band emission should absorb above the PL band or at most near the high PL energy side (Fig. 5). Apart from exciton binding energy ($\sim 0.15$ eV [15]), strong phonon coupling in the Si nanostructures [16] must be taken into account to explain such a shift between absorption and luminescence energies. One can also notice that in the OAE spectral region, sample A6520 absorbs more than sample A6510. At first sight, this demonstrates that the average crystallite size of A6520 is larger than that of A6510, this is in good agreement with the calculation results and would indicate the size-dependence of the OA in PS. In Fig. 6 we compare PL and OA of samples A6510 and E6510 which have almost the same thickness and concentrations of QWs and QDs, but having a slight difference in their mean crystallite size (cf. Table 2). The OAE of E6510 also lies approximately in the 1.8–2.6 eV spectral range. Taking into account the previously mentioned Stokes shift, when both absorption edges approach each other, the PL line shapes tend to coincide at the high PL energy side, where the contribution of QDs is more important (cf. Fig. 4). This suggests that in the spectral range where both OA coefficients coincide, absorption in A6510 and E6510 PS layers is dominated by QDs. This seems to be in good agreement with our calculation results (Table 2), where A6510 and E6510 PS samples have approximately the same QDs mean crystallite size; indeed, if we take into account the root mean square of both samples, we obtain a QDs size distribution almost similar at the high PL energy side (i.e., for smallest QDs).

However, below 2.2 eV A6510 absorbs less than E6510. This confirms the broad size distribution of E6510 which has larger crystallites, mainly QWs as suggested by our calculations (QWs of E6510 has a larger mean size accentuated by a more important root mean square, cf. Table 2). This observation is also consistent with the deviation of the PL line shape of E6510 from that of A6510 at the low PL energy side. Also, one should notice an exponential dependence of the OA coefficient between 1.8 and 2.6 eV (Fig. 6). This behaviour was explained elsewhere [17] like a phonon-assisted OA as expected from the indirect band gap of bulk c-Si. Further investigations are needed to explain the OA spectral behaviour below 1.8 eV, and to see whether excitonic transitions contribute to the total
OA in this spectral region. An estimation of the optical band gap from the OA coefficient $a$ and PL could constitute a fruitful method to further understand the PL emission process. To estimate the effective band gap from the PL line shape for each PS sample, we must subtract the surface effects from the PL spectra at the low PL energy side. This may easily be done in calculating the theoretical PL spectra, where only contributions of QWs and QDs to the PL spectrum are taken into account (cf. Fig. 4). The variation of the mean diameter $d_0$ for all QWs and QDs is around $3\sigma$ ($\sigma$ is the root mean square) [15]. Taking into account these considerations, the lowest PL energy corresponds to the largest QWs, whose size is about $(d_{0w} + 3\sigma)$. According to the PL model [5,11] the lowest PL energy is given by $E_{PL_{\text{min}}} = E_g - E_h + \Delta E$, where $E_g$ is the bulk silicon gap ($\approx 1.12$ eV), $E_h$ is the exciton-binding energy ($\approx 0.15$ eV [15]), and $\Delta E$ is the confinement energy in the largest QWs ($\Delta E = C_w(d_{0w} + 3\sigma)^{-1.39}$ in which $C_w$ is the confinement constant for QWs determined from the variation of the optical band gap versus the crystallite diameter [12]). The effective band gap determined from the PL spectrum is therefore $E_g^* = E_g + \Delta E$. In Table 3, we compare the optical band gap extrapolated from $(z\hbar\nu)^{1/2}$ with that calculated from the lowest PL energy. One may notice (Table 3) that the effective band gap of the PS samples obtained from OA measurements lies around 1.5 eV. Depth inhomogeneity may affect the value of the effective band gap determined from the OA coefficient especially for PS samples prepared in aqueous HF. However, PL shows that the effective band gap extrapolated from OA measurements approximately corresponds to that of the largest luminescent wires.

Furthermore one can notice that PL occurs in a spectral range over the effective band gap, where PS continues to absorb (Figs. 5 and 6). These results suggest that the lowest radiative transition between the conduction band and the valence band occurs in the largest luminescent wires and therefore the recombination process leading to the PL emission occurs in the c-Si crystallite core. According to the obtained results, the size-dependent spectral behaviour of PL and OA and the values of the band gap extrapolated from both of them (Table 3) suggest that photogeneration and radiative recombination occur in the c-Si core of the crystallites whose band gap is modified by the quantum-confinement effect. Hence, by using conventional techniques, such as PL and OA spectra measurements, and using a QCM, we demonstrate that the luminescence of PS arises from recombination between states confined inside the nanocrystallites, as has been directly proved by low-temperature resonant PL [6] and recently by “hole-burning” spectroscopy [7].

4. Conclusion

In this work, we have shown that during etching in aqueous HF, hydrogen bubbles may play an important role regarding the features and the morphology of the Si nanocrystallites forming PS. This may induce non-conventional PL shifts, which could be explained in a quantum-confinement model when all factors participating to PS formation are taken into account. According to a quantum-confinement based-PL model, we found that PL and OA are size-dependent and that their spectral behaviours depend on the shape and the size distribution of the c-Si crystallites. The value of the effective band gap energy determined from the lowest PL energy roughly corresponds to that extrapolated from the optical absorption coefficient, suggesting that the lowest radiative transition occurs in the largest luminescent wires within the c-Si crystallite core.

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References