

Kinetics of the photoinduced evolution of the nanostructured porous silicon photoluminescence

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Abstract

In this work we show that the illumination level used during porous silicon preparation is a key factor determining the subsequent photoinduced evolution of the photoluminescence spectra. The post-preparation evolution results from the combination of at least two effects. One of them is ruled by the size changes of the silicon nanostructure due to photo-oxidation, and dominates for samples prepared under low illumination levels. On the other hand, for samples prepared under high illumination levels the post-preparation evolution is dominated by a quenching effect, resulting from photoinduced dangling bonds generation in the hydrogen-rich surface of the nanostructure. The kinetics of dangling bond creation is similar to that found in the Staebler–Wronski effect for hydrogenated amorphous silicon. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The high specific surface of porous silicon (PS), useful for several technological applications, is also one of the principal factors for its instability [1]. The photoluminescence (PL) evolution after sample preparation strongly depends on the preparation conditions, which in turn involve many operational parameters. Some of these parameters are usually not considered relevant and remain uncontrolled. In particular, the illumination intensity used during preparation is generally not well specified. In this work we show that illumination during PS preparation is a key parameter which controls the post-preparation evolution of the PL. This fact may be responsible to a great extent for the reported differences on the PL spectra evolution of otherwise similar samples [2,3].

2. Experimental

Samples were prepared by anodic oxidation of n- and p-type silicon wafers. The p-type wafers, $\langle 100 \rangle$ oriented, had a resistivity in the range of 7–17 Ω cm. Two different n-type wafers were used: 1–10 Ω cm, $\langle 100 \rangle$ oriented, and 500–1500 Ω cm, $\langle 111 \rangle$ oriented. The electrolyte was composed of HF (50% solution) and absolute ethanol in a 1:2 volume ratio. The anodization currents were 10–20 mA/cm². Samples were prepared under tungsten-halogen lamp illumination. For n-type samples the intensity was 140 mW/cm², while for p-type samples intensities ranging from 0 to 140 mW/cm² were used.

Porous silicon samples were allowed to evolve under post-preparation light exposure (PPLE) with controlled conditions (wavelength: 400 nm, effective intensity: 1.35 mW/cm²). During the evolution, PL, ESR and IR spectra were recorded at different stages. PL spectra were recorded using a standard fluorometer, while the IR spectra were registered with a FTIR spectrometer as described elsewhere

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[3,4]. X-band ESR experiments (9.5 GHz) were performed at room temperature. Microwave power was 12.5 mW, modulation field 8 G, and modulation frequency 100 kHz.

3. Results and discussion

Fig. 1 shows the PL spectra of three p-type samples prepared under different light intensities. Each set of spectra shows the evolution during PPLE. Set A corresponds to a sample prepared using 12.1 mW/cm^2 . The initially intense PL band is gradually quenched during PPLE, maintaining its shape. This behavior is the same as for n-type samples, which require high intensity illumination (HII) during preparation in order to generate the positive carriers needed in the anodization reaction. However, the initial peak intensity for p-type samples prepared under HII is more than one order of magnitude higher than that of set A in Fig. 1.

Set C corresponds to low illumination level (5.9 mW/cm^2). As shown in the inset of Fig. 1, the behavior is the same as that reported in a previous work [3] for a sample prepared under ‘ambient conditions of temperature and illumination’. As shown in Ref. [3] there are two kinetically correlated components involved in the evolution of set C. The spectra of set B were obtained preparing the sample under an intermediate illumination level. The initial spectrum is a broad band peaking at around 633 nm, with a shoulder at around 590 nm. This initial band decreases during the first stages of PPLE, and after a certain time a single increasing band centered at 585 nm can be appreciated. As it will be shown latter, this behavior corresponds

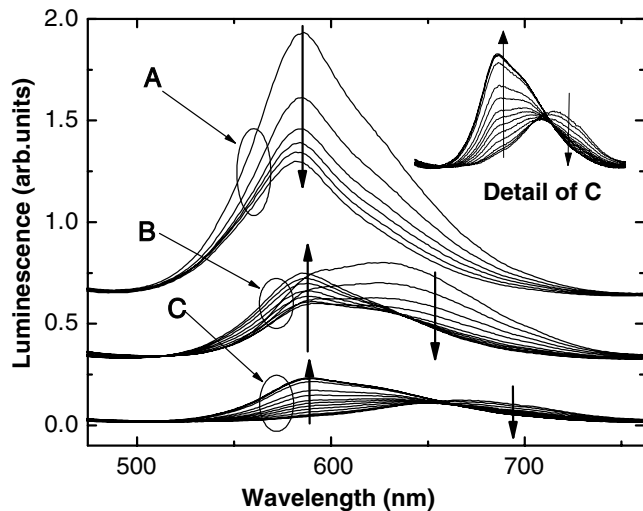


Fig. 1. Photoluminescence spectra for three PS samples prepared under different illumination levels, showing the post-preparation evolution. The post evolution set of spectra for each sample are grouped by a circle. The samples were made under the following illumination intensities (the total post evolution time are also indicated for each set): A: 12.1 mW/cm^2 (40 min), B: 8.1 mW/cm^2 (85 min), and C: 5.9 mW/cm^2 (80 min). Sets A and B have been shifted upwards for clarity. Vertical arrows indicate time evolution.

to an intermediate situation in which two simultaneous effects take place.

It should be remarked that all PS samples prepared under HII show PL spectra of similar shape and follow the same PPLE evolution kinetics, whatever the characteristics of the silicon, electrolyte, and preparation conditions. The intensities of the PL peak of a set of samples made under HII are shown in Fig. 2 in a log–log plot as a function of the post-preparation illumination time t_{III} . All samples included in this figure were prepared under 140 mW/cm^2 . The other preparation conditions covered the complete set of values indicated in Section 2. The values of the peak intensities are normalized to the as-prepared values. The PL intensity follows a power law $Y \propto (t_{\text{III}})^{\alpha}$, with α approximately $-1/3$ for all our HII samples.

The evolution of the PL of these samples resembles that of the photoconductivity of a-Si:H. The power law with exponent $-1/3$ strongly suggests a defect creation kinetics mediated by bimolecular carrier recombination, with carrier densities ruled by monomolecular recombination, as reported by Stutzmann, Jackson and Tsai (SJT) for amorphous silicon [5]. The SJT model predicts an evolution of the dangling bond (DB) density N as

$$N(t)^3 - N(0)^3 \propto tG^2, \quad (1)$$

where $N(0)$ is the DB density of the sample before illumination, t is the illumination time, and G is the electron–hole pairs generation rate.

We can assimilate the SJT model to the case of PS samples as follows. It is known that PS is a nanostructure made of quantum-wires-like nanocrystals, with a large hydrogen-rich surface [1]. This surface layer may be a defective region similar to a-Si:H. Therefore, we have nanocrystalline nuclei

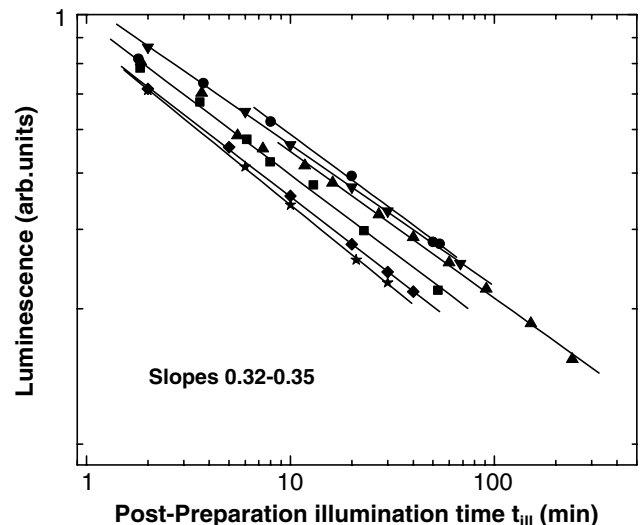


Fig. 2. Normalized photoluminescence peak intensities as a function of post-preparation exposure time for samples prepared under high intensity illumination (HII) starting from different silicon types, electrolyte compositions, and anodization conditions. Note that, despite the different preparation conditions, the behavior is the same for all the HII samples.

surrounded by a defective a-Si:H-like surface layer. Applying the quantum confinement model given in Ref. [3] to the initial spectrum of set A in Fig. 1, we obtained for the quantum wires an average width $L_0 = 2.40$ nm and rms deviation $\sigma = 0.14$ nm. As the recombination lifetime of carriers should be much larger in the nanocrystalline nuclei than in the defective surface layer, it can be assumed that the luminescence comes from radiative recombination in the nanocrystal, while non-radiative recombination mainly occurs in the surface a-Si:H-like layer. Therefore, the carrier densities in the crystalline nuclei of the nanowires should be ruled by non-radiative recombination in the surface layer, and the PL intensity will be proportional to the inverse of the defect density of the surface layer. Assuming that the hydrogen-rich surface layer behaves as a-Si:H during the PPLE, the DB density will increase following Eq. (1), and the PL will evolve as in Fig. 2.

In order to verify the validity of this photoinduced DB creation model, we performed ESR measurements following the evolution during a PPLE experiment of a PS sample prepared under HII. A tungsten-halogen lamp was used as light source, with a hot mirror to avoid heating. The resulting intensity over the PS surface was around 60 mW/cm^2 . The g factor associated to the ESR spectra was $g = 2.0055$, which corresponds to DB [6]. Peak-to-peak amplitudes of the derivative spectra were used to evaluate the relative density of spins. The results of applying Eq. (1) to the measured spin densities are shown in Fig. 3 as a function of the illumination time t_{ill} . Light coming from a blue light source (1.5 mW/cm^2 –400 nm) produces similar results, although the evolution is slower. As shown in Fig. 3, the DB density of PS also evolves following the SJT model. Therefore, the results of photoinduced evolution of PL and ESR spectra of PS samples prepared under HII suggest that a mechanism similar to that of the Staebler–Wronski [7] effect takes place in the hydrogen-rich surface of PS. However, the PL quenching effect is not recovered after annealing in vacuum at around 200°C during more than

1 h. Moreover, we found that the IR modes related to Si–H bonds significantly decrease after illumination in vacuum, showing photoinduced hydrogen loss, in agreement with Ref. [8].

The kinetics of the PL evolution during PPLE can be explained as a consequence of the simultaneous action of two effects. One of them, the photo-oxidation, which reduces the width of the quantum wires of the PS structure changing the confinement gap (as we explained in a previous work [3]), dominates for samples prepared under low illumination levels. The other effect, which is significant for samples prepared under HII, is the above mentioned photoinduced quenching. Using ESR we measured the initial DB density $N(0)$ for samples prepared under the two extreme illumination conditions. $N(0)$ of samples prepared in darkness is 1.7 times larger than that of samples prepared under HII. This result is in agreement with the above interpretation: samples prepared under low illumination levels are more defective and thus have a lower PL intensity than those prepared under HII, as observed in Fig. 1. Moreover, the as-prepared PL spectra of low illumination levels samples peak at larger wavelength, indicating larger average widths of nanowires.

We performed two additional experiments in order to test our assumptions separating the two mentioned effects. In order to preclude photo-oxidation, a sample prepared under HII was kept in vacuum (10^{-7} Torr) and subject to a PPLE experiment in these conditions. A quenching similar to that of Fig. 1 A was observed. Subsequent IR measurements confirmed hydrogen photoeffusion effects. Then we performed a second PPLE experiment in air on the same sample, allowing photo-oxidation, and a behavior like that of Fig. 1 C was appreciated, because the initially large PL signal had been quenched in the first experiment. Therefore the behavior of set B in Fig. 1 can be attributed to the simultaneous action of the two previously cited effects. We will report and discuss more extensively the results of these experiments in a forthcoming publication.

4. Conclusions

In this work we presented experimental results showing that illumination conditions during electrochemical preparation of porous silicon are a key factor determining its post-preparation behavior. We found that there are two simultaneous photoinduced effects during post-preparation illumination. Photoinduced evolution of the PL spectra of samples prepared using low illumination levels is dominated by photo-oxidation effects, whereas for samples prepared under high illumination levels the dominating effect is a photoinduced quenching produced by dangling bond generation. The quenching follows a similar kinetics as the Staebler–Wronski effect of a-Si–H photoconductivity. However, the microscopic mechanism involved seems to be different, as the effect is not reversible, probably as a consequence of the measured photoinduced hydrogen effusion. ESR measurements agree with the above proposed explanation.

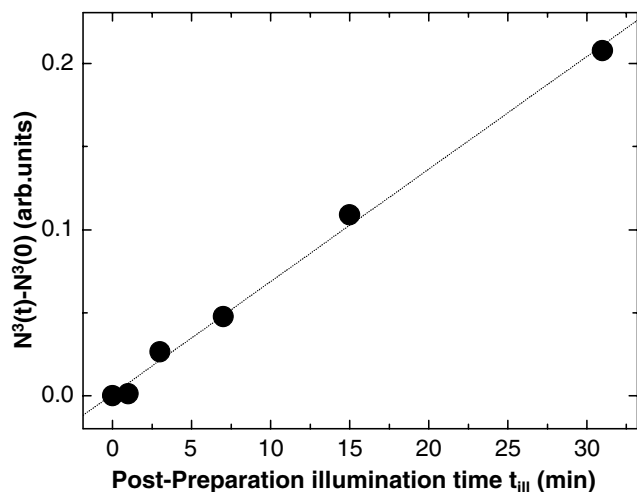


Fig. 3. Time dependence of the photoinduced dangling bond density, according to Eq. (1). The linear behavior confirms the proposed model.

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