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Photoluminescence of monocrystalline and stain etched porous silicon doped with high temperature annealed Europium

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ABSTRACT

In this work, for the first time the photoluminescent emission and excitation spectra of non-textured layers and stain etched porous silicon layers (PSLs) doped with high temperature annealed Europium (Eu) are evaluated. The PSLs are evaluated as host for rare earth ions and as antireflection coating. The applied doping process, which consists in a simple impregnation method followed by a high temperature annealing step, is compatible with the standard processes in the fabrication of solar cells. The results show down-shifting processes with a maximum photoluminescent intensity at 615 nm, related with the transition ${}^5D_0 \rightarrow {}^7F_2$. Different initial concentrations of $\text{Eu}(\text{NO}_3)_3$ were evaluated to study the influence of the rare earth concentration in the photoluminescent intensity. The chemical composition and the morphology of Eu-doped PSLs are examined by means of X-ray Dispersion Spectroscopy, Fourier Transform Infrared Spectroscopy, and Scanning Electron Microscopy. These Eu-doped layers are

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considered to be applied as energy converters in silicon-based third generation solar cells.

Keywords: Porous Silicon; Monocrystalline Silicon; Europium doping; Photoluminescence; Down-Shifting; Solar Cells

Pacs: 68.37.Hk; 78.30.Hv; 78.55.Mb; 88.40.hj

1. Introduction

Rare earths **ions** are being considered as luminescent materials to enhance the performance of solar cells [1]. This improvement can be achieved by means of down-conversion, up-conversion, and down-shifting processes. A down-conversion (DC) layer placed on the frontal side of a solar cell can generate two low-energy photons from a high-energy photon, avoiding thermalization losses. Up-conversion (UC) layers are normally placed in the rear side of the solar cell, generating a photon within the silicon band gap, from two low-energy photons. Luminescent down-shifting layers (DS) are formed with the aim of absorbing photons in the 300-500 nm range, and re-emit them at wavelengths where the solar cell exhibits a higher spectral response [2].

In recent works, it has been observed that the Eu^{3+} ions can be used to exploit and down-shift photons under 400 nm and re-emit them at 612 nm, close to the maximum quantum efficiency wavelength of crystalline silicon based solar cells [3]. This makes Eu^{3+} ions an ideal candidate to improve the spectral response of crystalline silicon solar cells.

There are several techniques to insert rare earth ions in silicon to produce UC, DC and DS when are used as substrates in solar cells. One of them is placing the rare earth ions

in the encapsulating polyvinyl acetate (PVA) [3]. Another approach is to incorporate the rare earth ions in the antireflection coating formed on the crystalline silicon substrate [4, 5].

The incorporation of the rare earth ions in silicon can be carried out by ion implantation [6], electrochemical migration [7] or spark processing [8] and even sol-gel processes [9]. However the high cost of these techniques or the required time of the processes is not adequate for the solar cells fabrication process. For this reason, the thermal doping process is one of the most affordable methods to incorporate Eu^{3+} in silicon. Other advantages of this thermal process are its simplicity and the ability to easily control diffusion parameters through time and temperature.

However, to obtain a cost-effective doping process in silicon is complicated. One of the most promising alternatives to the conventional silicon doping procedures is to use porous silicon layers (PSLs) [5, 10] as rare earth host because of their large surface area, allowing easy penetration of the ions into the matrix. These layers also have anti-reflection properties, which make them ideal candidates to improve the light absorption in silicon-based optoelectronic devices [11].

PSLs can be formed by electrochemical anodization of silicon in HF-based solutions [12] or stain etching in HF/HNO₃ mixtures [13]. The electrochemical etching of silicon presents some disadvantages for its utilization at industrial level, as the need of high anodic currents [14], and the difficulty of achieving an uniform and protected (from acid infiltration) back-side electrode in large areas to produce electrochemical etching. These disadvantages are not presented in the stain etching process, as the porous layers are formed by simple immersion in the HF/HNO₃ solution [15].

The photoluminescent properties of the electrochemically etched porous silicon doped with Eu^{3+} have been previously studied [16-18]. The incorporation of Eu^{3+} ions to the substrate consists in two steps, impregnation and annealing, as the method used in this work. But when an electrochemical method is used to produce the PSLs, the impregnation method employed requires longer times, compared to the stain etching process. The oxidation is present in the doping method described in this study for stain etched samples, and it is necessary to enhance the luminescence [4].

In this work the photoluminescent emission (PL) and photoluminescent excitation properties of Eu^{3+} incorporated in stain etched PSLs and non-textured layers are evaluated for photovoltaic applications, employing a low cost method that could improve the photoconversion efficiency of crystalline silicon solar cells [2].

2. Experimental

The PSLs were formed by stain etching of 1x1 cm p-type Cz **(Czochralski)** silicon substrates with resistivity between 0,8 – 1,2 $\Omega\cdot\text{cm}$, in HF/HNO_3 aqueous solution. Low concentration of HNO_3 and short etching time were used, in order to assure the homogeneity of the porous surface [19]. After the stain etch process, the samples were rinsed in deionized water, and subsequently dried under N_2 flux. The non-textured layers were formed submitting the samples to saw damage etching by immersion in a NaOH solution.

To dope the PSLs and the non-textured samples, Eu (III) nitrate hexahydrated salt was diluted in pure ethanol to obtain different molar concentrations. The samples were mainly doped with **a solution** 0,5M $\text{Eu}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$. A drop with this solution was deposited in the center of each sample, and homogeneously distributed across the surface by a spin-on procedure.

Finally, the samples were submitted to a thermal process in a conventional furnace, at 850° C for 50 min. Although other diffusion temperatures and times have proven to be efficient to incorporate and activate rare earth ions in silicon [4], only parameter ranges suitable to be introduced in a solar cell fabrication process were chosen to study the PL properties.

The chemical composition of the stain etched PSLs was analyzed by means of a Fourier Transform infrared spectrometer (FTIR) model Bruker Tensor 27, using 4 cm⁻¹ resolution. The elemental composition and the morphology of the Eu-doped stain etched PSLs were examined by means of X-ray dispersion spectroscopy (EDS) and scanning electron microscopy (SEM) in a JEOL 6300 electron microscope.

The UV-Vis photoluminescence measurements were obtained exciting the samples with light from a 300 W Xe arc lamp, passed through a 0,25 m double-grating monochromator and detected with a 0,25 m monochromator and a photomultiplier tube. All spectra were acquired at room temperature. To compare the PL intensities, a sample holder was used to assure the same emplacement of the samples, the optical path was kept unaltered and the monochromator slits remained unchanged. The total hemispherical reflectance was measured with a Varian 500 spectrometer equipped with an integrating sphere.

To calculate the internal quantum efficiency (IQE), light selected in different spectral ranges by a set of filters was focused on the samples, and the short circuit current was measured by an amplifier which adjusts a zero voltage directly at the sample.

Furthermore, the setup included some bias light lamps, which produced an additional steady state white light illumination with the aim of achieving the standard operating conditions of a solar cell.

3. Results and discussion

The FTIR spectra in figure 1 show the absorption bands corresponding to the vibrational modes of the Si-O bonds at 1100 cm^{-1} and 1185 cm^{-1} for Eu-doped PSLs, and at 1078 cm^{-1} for the Eu-doped non-textured layer. The shift and broadening of the Si-O absorption band for Eu-doped PSLs are the result of a combination of the asymmetric stretching of the LO3-TO3 mode [20] and the inverted oxide LO4-TO4 mode [21], which confirms the amorphous characteristics of the SiO₂ on the surface. Besides, the peak from the non-textured layer at 1078 cm^{-1} corresponds to the Si-O vibrational mode [22], which confirms the presence of a highly ordered SiO₂. This oxidized silicon acts as a host for activated Eu³⁺ ions, contributing to the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$. Also the ordered SiO₂ produces the splitting of the PL at 615 nm, detected in figure 2.

A SEM image of a Eu-doped PSLs surface with the maximum initial nitrate solution at 1500x is shown in figure 3 (a). As the result of the spin-on process, the surface is completely covered by the nitrate solution which, after the thermal process, is also covered by residual salts. To incorporate this process to a photovoltaic manufacturing line, it is necessary a silicon surface completely free of residual salts from the rare earth doping process, to place the electrical contacts and the passivation layer. Consequently, PSLs Eu-doped with the same procedure were cleaned in order to remove the residual salts and it is shown in figure 3 (b). This cleaning procedure could also enlarge the pore size on the silicon surface, as it is observed comparing figures 3 (a) and 3 (b).

The EDS spectrum of figure 4 shows the elemental composition of the Eu-doped PSLs after the cleaning process. The Eu peaks observed confirm the presence of Eu³⁺ ions over the PSLs surface, and the presence of F is derived from the HF acid used to remove the oxide layer formed during the cleaning process.

Figure 2 also shows the normalized emission spectra of the Eu^{3+} optically activated in the PSLs and in non-textured samples. The spectra were measured in the range of 450 to 750 nm, upon excitation of the $^5\text{L}_6$ level (at 394 nm). All the observed peaks are attributed to the transitions from the $^5\text{D}_0$ level to the spin-orbit states of $^7\text{F}_j$ ($j=1,2,3,4$). Unlike the Eu^{3+} doped PSLs formed by electrochemical anodization [16], there is no emission corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition, characteristic of high crystalline substrates, like silicon nanocrystallites [16]. There are no appreciable emissions corresponding to transitions $^5\text{D}_{1,2} \rightarrow ^7\text{F}_j$ between 450 and 570 nm, indicating that the dominant relaxation process among the $^5\text{D}_j$ levels in these silicon substrates is the multi-phonon de-excitation [9]. The emission bands are within the 575 – 725 nm range, where the crystalline silicon solar cells present an optimum spectral response [2]. Also, there are not intraconfigurational 4f-4f transitions from the ground $^7\text{F}_0$ level that absorb light between 550 and 1100 nm, so the wavelengths in the regions of the solar spectrum that are not down-shifted are transmitted to the underlying substrate.

The most intense peak at 615 nm in Eu-doped PSLs and 611 nm in the non-textured layer corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. This transition is hypersensitive to the local environment of the Eu^{3+} ions, and it could be used as a spectroscopic probe of the environments around the Eu^{3+} ions. As a consequence, the changes in this transition in the non-textured layer reveals the existence of optically activated Eu^{3+} in sites with different symmetries, due to differences in the local symmetry around the Eu^{3+} ions [8, 23]. This result could indicate that activation of Eu^{3+} ions in the non-textured layer occurs not only in the crystalline silicon matrix, but also in the top oxide layer formed during the thermal process [4]. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in the PL spectrum of the PSLs is wider and does not split, suggesting that the activation of Eu^{3+} ions occurs in a large variety of sites: the crystalline silicon matrix and different sites in the amorphous layer

formed on the surface of the PSLs [24]. This result differs from the same transition in the emission spectrum of Eu^{3+} doped PSLs formed by electrochemical anodization [16], which present a $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition split.

Figure 5 shows a comparison of the Eu^{3+} photoluminescent emission intensities for the Eu-doped substrates under study, upon excitation at 394 nm ($^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition). The integrated intensity ratio of the non-textured layer and stain etched PSLs emission spectra between 550 and 750 nm is 12,51. The inset in Figure 5 shows the reflectance spectra of the undoped stain etched PSLs and the non-textured layer. As it can be observed, the reflectance values between 300 and 550 nm are very low for the stain etched PSLs, producing larger absorption of the high-energy photons that can be photoconverted than for the non-textured layer [25]. On the other hand, several studies of external quantum efficiency from light-emitting diodes with textured surface [26, 27] demonstrate that the texturing of the semiconductor surfaces increases the external quantum efficiency. Consequently, we conclude that the internal PL is lower for the Eu-doped stain etched PSLs compared to the non-textured sample. This conclusion would indicate that most of the Eu^{3+} ions incorporated in the stain etched PSLs have not been activated or their photoluminescence has been quenched [28].

Figure 6 shows the integrated PL intensity of Eu-doped PSLs samples as a function of the initial concentration of the europium nitrate solution. The PL intensity increases, and shows no evidence of a concentration quenching effect in a wide range of initial molar concentrations. The intensity has an exponential dependence with the initial Eu^{3+} . However, for concentrations higher than those of figure 6, the deposited solution drop is not spreading over the whole sample in the spin-on procedure, due to its high viscosity. Further experiments should be carried out to decrease the solution viscosity in order to increase the Europium concentration using spin-on processes.

The excitation spectra of the Eu^{3+} doped PSLs and non-textured layers, measured between 300 and 550 nm are shown in Figure 7. The excitation spectrum corresponding to the stain etched and Eu-doped PSLs was normalized to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition (395 nm), and measured at $\lambda_{\text{em}} = 615$ nm, where it presents the maximum photoluminescent intensity, and the excitation spectrum corresponding to the Eu-doped non-textured sample was normalized to the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition (465 nm), and measured at $\lambda_{\text{em}} = 611$ nm (also at its maximum photoluminescent intensity). For both stain etched PSLs and non-textured samples, the excitation spectra present characteristic bands corresponding to the ${}^7\text{F}_0 \rightarrow {}^5\text{H}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}^3$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ transitions.

To evaluate which sample can offer a higher contribution to the enhancement of a solar cell efficiency, the increase of the e-h pairs produced by the down-shifting process in a crystalline silicon solar cell has been approximated considering only the emission at the maximum photoluminescent intensities at 615 nm for stain etched Eu-doped PSLs and 611 nm for the Eu-doped non-textured layer.

The photons down-shifted to 615 nm and 611 nm by the Eu doped PSLs and the Eu-doped non-textured layer, respectively, have spectral distributions that can be determined by the excitation spectra.

Taking into account this spectral distribution of down-shifted photons and a typical internal quantum efficiency (IQE) of a crystalline solar cell, it could be estimated the gain of photons in the range of 350-550 nm that are converted in electron-hole pairs with respect to the non doped layers.

Then, the IQE is defined as the relation between the e-h pairs produced and the incident non-reflected photons, as function of the wavelength λ :

$$IQE(\lambda) = \frac{N(\lambda)}{\varphi(\lambda)} \quad (1)$$

where $N(\lambda)$ is the density of e-h pairs generated and $\varphi(\lambda)$ is the density of incident non-reflected photons.

As the incident photons are transformed to down-shifted photons at 615 and 611nm for Eu-doped PSLs and non-textured layers, respectively, the e-h pairs produced by these down-shifted photons can be estimated with equation (1) for both Eu-doped layers:

$$N_{Eu,PSL}(\lambda) = \varphi_{Eu,PSL}(\lambda) \cdot IQE(615nm) \quad (2)$$

$$N_{Eu,non-textured}(\lambda) = \varphi_{Eu,non-textured}(\lambda) \cdot IQE(611nm) \quad (3)$$

Consequently, the increase of e-h pairs due to down-shifting processes in the 350 – 550 nm spectral range can be estimated for the Eu^{3+} doped stain etched PSLs by:

$$\frac{N_{Eu,PSL}}{N_{PSL}} = \frac{\int_{350}^{550} \varphi_{Eu,PSL}(\lambda) \cdot IQE(615nm)d(\lambda)}{\int_{350}^{550} \varphi_{Eu,PSL}(\lambda) \cdot IQE(\lambda)d(\lambda)} \quad (4)$$

and for the Eu^{3+} non-textured layer:

$$\frac{N_{Eu,non-textured}}{N_{non-textured}} = \frac{\int_{350}^{550} \varphi_{Eu,non-textured}(\lambda) \cdot IQE(611nm)d(\lambda)}{\int_{350}^{550} \varphi_{Eu,non-textured}(\lambda) \cdot IQE(\lambda)d(\lambda)} \quad (5)$$

The IQE spectrum employed for the calculations is shown in figure 8 (a), and it corresponds to a typical crystalline silicon solar cell [29]. The increment of e-h pairs generated by down-shifting processes by the Eu^{3+} stain etched doped PSLs and non-textured layer compared to the non-doped ones are shown in figure 8 (b), and have been calculated with equations 4 and 5, integrating numerically. Then, for the stain etched

Eu-doped PSLs, the estimated increment in e-h pairs generated by the fraction of the photons down-shifted by the Eu^{3+} photoconversion layer (to 615 nm) is + 35,46% compared to non-Eu-doped PSLs, and for the Eu-doped non-textured layer (to 611 nm) is + 25,65% compared to a non-Eu-doped non-textured sample.

It should be taken into account that these quantitative results are an estimation of the maximum percentage of IQE increment that could be obtained for the light in the spectral range down-shifted by europium in doped cells compared to non-doped ones. In a more complex model, other factors could play a role as, for example, the interaction of europium ions and the silicon nanostructures embedded in the PSLs and the possible recombination processes through the introduction of energy levels in the band gap, which should be further studied.

4. Conclusions

In this paper, a novel low cost and compatible method with the silicon-based solar cells fabrication procedure has been employed in order to incorporate and optically activate Eu^{3+} ions into a layer with antireflection properties formed by acid texturization and into a non-textured layer.

The excitation and emission spectra show that these layers absorb high energy photons, between 300 and 550 nm, and down-shift them to wavelengths close to the maximum quantum efficiency wavelength of crystalline silicon solar cells. Consequently, this process may improve the spectral response of this type of solar cells.

There is no evidence of quenching effect on the emission intensity within the range of Eu^{3+} doping concentrations studied. Also, the PL intensity in Eu-doped PSLs has an

exponential dependence with the Eu^{3+} concentration. Thus, the PSLs are adequate Eu^{3+} hosts, allowing the penetration by thermal diffusion of Eu^{3+} ions.

On the other hand, the down-shifting effect of Eu^{3+} can enlarge the internal quantum efficiency of a silicon-based solar cell with stain etched Eu-doped PSLs on the front side compared to the same solar cell with a Eu-doped non-textured layer on the front side. However, in our experiments the higher photoluminescent intensity corresponds to the Eu-doped non-textured layers, suggesting that a lower quantity of ions has been optically activated in the PSLs compared to the non-textured layers. Further experiments should be carried out in order to increase the photoluminescent intensity of the Eu-doped PSLs.

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Figure captions

Figure 1: FTIR transmission spectra of Eu^{3+} stain etched doped PSLs and a non-textured Si layer.

Figure 2: Photoluminescence spectra excited at $\lambda_{\text{ex}} = 394$ nm of stain etched Eu-doped PSLs and a Eu-doped non-textured layer. The intensities of the PL are normalized to the respective main emission peak ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ for comparative purposes. The samples were doped with an initial concentration of 0,5M $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

Figure 3: SEM images of (a) the stain etched Eu-doped PSLs surface just after the diffusion process and (b) the same surface after the cleaning process.

Figure 4: EDS spectrum of the stain etched Eu-doped PSLs after the cleaning process.

Figure 5: Comparison of photoluminescence emission intensities of stain etched Eu-doped PSLs and a Eu-doped non-textured layer. The inset shows the reflectance spectra of both undoped substrates between 300 and 1200 nm. The samples were doped with an initial concentration of 0,5M $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

Figure 6: Evolution of the PL intensity for the stain etched Eu-doped PSLs samples as a function of the molar concentration (M) of Eu^{3+} in the initial nitrate solution.

Figure 7: Photoluminescent excitation spectra for stain etched Eu-doped PSLs ($\lambda_{\text{em}} = 615$ nm) and for a Eu-doped non-textured layer ($\lambda_{\text{em}} = 611$ nm). The intensities of the PL are normalized to the transition ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$. The samples were doped with an initial concentration of 0,5M $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

Figure 8: (a) IQE spectrum of a typical crystalline silicon solar cell; and (b) e-h pairs generated from photons in the range of 350-550 nm that are transformed to 615 nm

photons by the stain etched Eu-doped PSLs, and to 611 nm by the Eu-doped non-textured sample.