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Excitation mechanisms and localization sites of erbium-doped porous silicon

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Porous silicon (PS) is doped with erbium by electrochemical anodisation. The penetration of erbium into the PS layer is confirmed by Rutherford backscattering spectroscopy (RBS) and energy dispersive X-ray (EDX) measurements. Efficient green and infrared emissions were observed at room temperature. The investigations are focused on the evolutions versus temperature and pump intensity of the green photoluminescence (PL) corresponding to the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition. It was found that an erbium related level defect can be involved on the excitation and emission processes of erbium. Pump intensity dependent PL studies revealed that for the electrochemical incorporation, most of the Er^{3+} ions are localized inside the Si nanocrystallites and not in stoichiometric SiO_2 . The optical cross-section is close to that of erbium in Si nanocrystallites.

Keywords: Porous silicon; Erbium; Excitation mechanisms; Cross-section

1. Introduction

Erbium-doped silicon has been studied for over a decade for possible applications in optoelectronics and in telecommunication because erbium can emit photons at 1.54 μm due to an intra 4f shell transition between the $^4I_{13/2}$ and the $^4I_{15/2}$ levels. This emission is particularly attractive since its wavelength falls inside a window of maximum transmission for silica optical fibers. The development of practical, silicon-based

light emitting devices, however, has been severely limited by a low erbium concentration and strong quenching of photoluminescence (PL) intensity. Several alternative ways are currently being pursued in order to deal with its inability to luminescence efficiently. Porous silicon (PS) is considered an appropriate material for erbium doping because its visible PL is efficient and is compatible with standard silicon processes in making integrated optoelectronic devices [1]. Its very large surface area to volume ratio makes the PS matrix very accessible for erbium doping, as well as a host for large concentrations of oxygen necessary for erbium emission. Doping of PS

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with rare-earth (RE) ions has been achieved by ion implantation [2], diffusion [3], dip-coating [4] and electrochemical deposition [5,6]. Cathodic electrochemical deposition is preferred because it offers the advantages of deeper erbium penetration (10–20 μm), lower cost, and simplicity of processing. The question here is where in PS are located Er^{3+} ions, when PS consists of various crystalline and amorphous phase, and how Er^{3+} ions are excited from the c-Si nanocrystallites?

In this work, we have doped PS with erbium by electrochemical deposition. Erbium profile in the PS layer is studied from the Rutherford backscattering spectroscopy (RBS) and energy dispersive X-ray (EDX) measurements. The dependencies of PL intensity versus temperature and pump intensity are investigated. The processes of erbium excitation and de-excitation in porous silicon are discussed.

2. Experimentation

We used PS samples prepared by anodising a p-type (1 0 0) silicon substrate (0.7–1.3 $\Omega\text{ cm}$) in a mixture of HF (40%) and ethanol (HF:C₂H₅OH = 1:1)

with a current density of 12 mA/cm^2 . The anodisation time is chosen to obtain a PS thickness less than 4 μm . Using the gravimetric method, the porosity of the PS layer is estimated to 65%.

Erbium is introduced into the PS by electrochemical deposition from a saturated chloride solution of erbium ($\text{ErCl}_3\text{:C}_3\text{H}_5\text{OH}$) for 30 min at a current density of 0.1 mA/cm^2 . After erbium deposition, the sample is rinsed with ethanol in order to clean the surface, and then is subjected to two classic thermal annealing (CTA) at 300 $^\circ\text{C}$ for 30 min and at 1000 $^\circ\text{C}$ for 20 min to activate the erbium ions in the matrix.

In order to study the incorporation of erbium in the PS, the penetration was controlled by Rutherford backscattering spectroscopy (RBS) of $^4\text{He}^+$ ions delivered by a 2 MeV Van de Graf accelerator and energy dispersive X-ray (EDX) analysis.

Photoluminescence (PL) measurements are performed by using the 488 nm Ar^+ line as excitation source, a triple monochromator for light analysis and a “GaAs” photomultiplier. For infra-red PL measurements, an InGaAs photodiode is used. The sample temperature was controlled from 20 to 300 K by a closed cycle He cryostat.

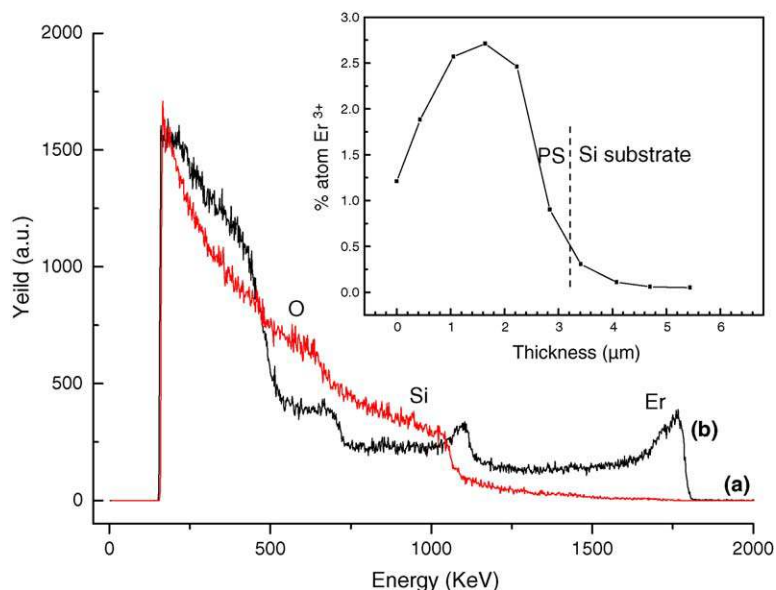


Fig. 1. RBS spectra of porous silicon (a) and erbium-doped porous silicon (b). Inset: concentration of erbium, deduced from EDX analyses, in different region of the PS layer.

3. Results and discussion

Fig. 1 presents the RBS spectra of undoped PS layer and the same PS layer doped erbium after subsequent annealing. The energies corresponding to erbium, silicon, and oxygen located at the sample surface are indicated. The high energy position (1200–1780 keV) is related to erbium profile into the PS layer. It is clear from the figure that erbium concentration increases from the top surface of the PS layer and is quite constant in the middle part. Further informations on erbium incorporation on the host are given from EDX measurements performed on SEM cross-section of the PS layer (inset of Fig. 1). The results show that the atomic percentage of erbium increases from 1.4% at the top region of the layer to 2.7% at the middle part and then decreases to 0.2% at the interface PS/Si. These results are in agreement with the RBS measurements.

Fig. 2 shows the PL spectra, in the visible and IR regions of erbium-doped PS after annealing at 1000 °C in air. The relatively strong transitions at 18,500 cm⁻¹ (0.540 μm) and 18,235 cm⁻¹ (0.548 μm) correspond to the green emissions from the ²H_{11/2} and ⁴S_{3/2} levels to ⁴I_{15/2}, respectively. The IR PL peaks localized at 0.98 and 1.53 μm correspond to the ⁴I_{11/2} → ⁴I_{15/2} and ⁴I_{13/2} → ⁴I_{15/2} transitions, respectively. The PL band at 1.14 μm is relative to IR emission from bulk Si. These results prove the existence of erbium into the PS layer. The PL peaks are not well resolved indicating that probably erbium activation in the host is not completely performed or the Er³⁺ ions occupy multi-sites in Si nanocrystallites and other part of the ions are dispersed in the SiO_x phase. Oxygen atoms may be effectively incorporated deep into the pores of porous silicon and Er–O complexes may be formed [7].

Erbium ions can be located in c-Si nanocrystallites or in the untiring amorphous SiO_x phases. In both cases, energy transfer can occur to erbium ions. It is known that in ordered semiconductor, RE ions create trap level localized in the band gap. RE excitation is a result of the thermalisation of carriers localized at RE trap level [8]. For Er³⁺ in amorphous SiO_x, excitation transfer occurs because the ions are located within a few nanometres of the c-Si nanocrystallites. The formed excitation inside the c-Si nanocrystallites can be subsequently transferred to the erbium ion.

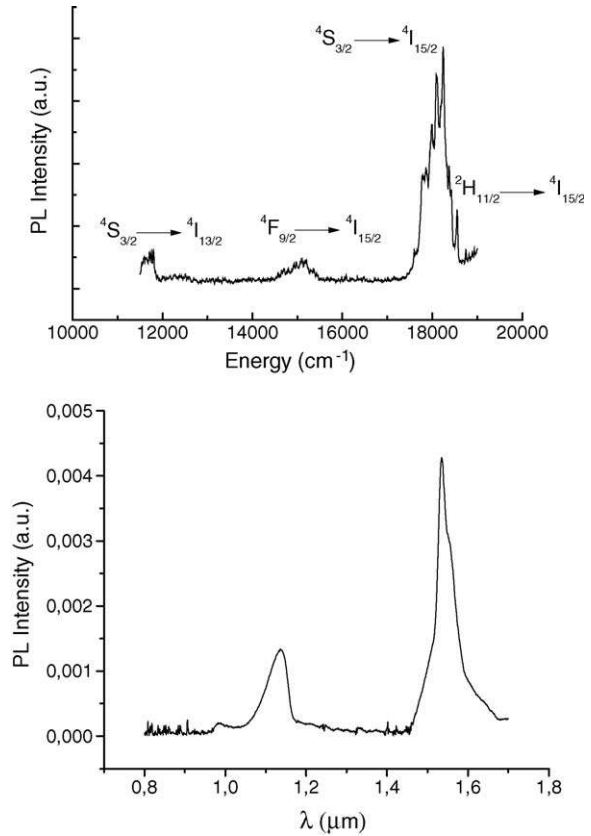


Fig. 2. PL spectra of erbium-doped PS, at room temperature after annealed at 1000 °C, in the visible and IR ranges.

The evolution of the PL intensity relative to the ⁴S_{3/2} → ⁴I_{15/2} transition is studied versus temperature. The PL intensity is kept practically constant at low temperature and quenches significantly with increasing temperature. Such temperature behaviour is a result of the thermalisation of carriers localized at erbium trap level [8,9] indicating a crystalline environment of Er³⁺ ions. Thus, it seems that most of Er³⁺ ions in the PS matrix are located in the c-Si nanocrystallites.

The PL intensity I at 18,235 cm⁻¹ for erbium-doped PS depends on temperature and is given by [8–10]:

$$I \propto \frac{N\tau}{\tau_{\text{tr}}\tau_{\text{rad}}[1 + W \exp(-E/KT)]} \quad (1)$$

where τ is the PL lifetime of erbium, τ_{rad} , the radiative lifetime of the ion, τ_{tr} , the lifetime required for energy transfer and τ is the lifetime of erbium. E is the energy gap between the conduction band and the erbium related level. W is defined as $W = \sigma_n n_c / \sigma_p G \tau_c$, with τ_c being the carrier lifetime and n_c being the density of state at the bottom of the conduction band, G , the optical generation rate of e-h pairs, and σ_p , σ_n are the capture cross-section for electron and holes, respectively.

Fit of this Eq. (1) to the data in Fig. 3 is shown as solid line. It is evident that Eq. (1) has the right functional form to describe the experimental results. In fact the intensity I has a constant value at low temperatures while at higher temperatures it decreases with an activation energy E of 0.206 eV. For erbium doping crystalline silicon, the value of E measured by DLTS analysis is 0.15 eV [8]. In other work [9], the authors have shown that for erbium-doped PS (using the implantation technique) the activation energy is $E = 0.104$ eV. The defect induced energy level at $E = 0.206$ eV below the conduction band constitute a trap for the photogenerated carriers and bound excitons are formed. The energy of the recombined excitons is subsequently transferred to the Er^{3+} 4f-shell. At low temperature, we assist to the formation of bound excitons and energy transfer to Er^{3+} . However, with increasing the temperature, the formed bound exciton can be dissociated which reduces the excitation efficiency. The energy backtransfer from an excited Er^{3+} to a trapped carrier state decreases the excited state lifetime, and with it the luminescence efficiency. Quenching can also occur by Auger energy

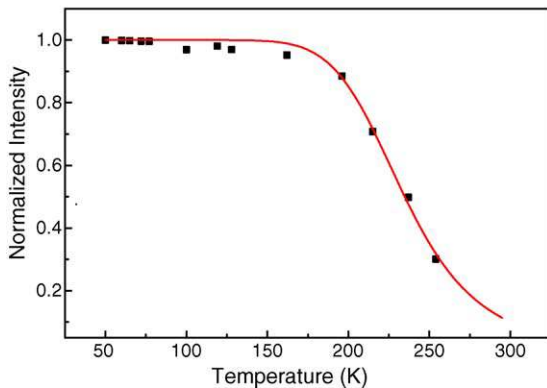


Fig. 3. PL intensity of erbium in PS as a function of temperature, the solid line is the best fit from Eq. (1).

transfer to free carriers [11], if these are present in sufficiently high concentration. We note that both exciton dissociation and backtransfer processes are phonon-assisted. In this study (PS:Er) the PL quenching with temperature is relatively important because the energy E is approximately only three times the energy of a TO phonon of PS, so, the probabilities of exciton dissociation and backtransfer increase with temperature. The excitation mechanism of Er^{3+} in PS is summarized in Fig. 4.

$E = 0.206$ eV is comparable to that in c-Si substrate (0.15 eV) so, the thermal quenching of PL intensity is important. This can be explained by a deeper incorporation of erbium from electrochemical method as shown from RBS and EDX measurements. For the immersed method, the thermal quenching of both PL intensity and PL lifetime were found to be weak [12] compared to the implanted technique. The authors [12] suggest that erbium-doped in PS from the immersed method is located at the surface of PS.

We have shown in previous work that energy transfer from PS to Eu^{3+} or Tb^{3+} is not the principal route for radiative transition [4,13]. This is because Eu^{3+} and Tb^{3+} ions are incorporated with the immersed method, so RE ions are localized essentially in the PS surface which is dominated by stoichiometric SiO_2 . Consequently no evidence of carrier-mediated excitation was reported for either Eu^{3+} or Tb^{3+} luminescence. The c-Si nanocrystallites in the surface have small size than those into the layer. As the band gap increases with size decrease of c-Si nanocrystallites,

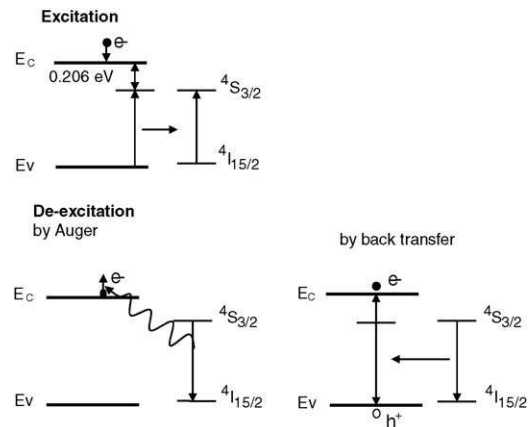


Fig. 4. Schematic of excitation and emission processes in erbium-doped PS.

we think that the Er^{3+} -related level defect is localized deeply in the gap which can limit the processes of exciton dissociation and backtransfer because the phonon energy is weak compared to the value of E in this case. As it has been shown for implanted method, in the present study, Er^{3+} ions are located essentially in the Si crystallites of the middle part of the layer. The band gap of these crystallites is not important relatively to the band gap of c-Si substrate. It is known that thermal quenching depends strongly on the band gap of the semiconductor because as the band gap is large as the energy E of RE related defect increases, which reduces the back transfer and Auger quenching processes.

To gain further insight into the excitation mechanism of erbium ions in PS, study of the dependence of the PL intensity on the pump intensity, is performed (Fig. 5). The green PL intensity increased nearly linearly for low pump intensity and saturation was observed at pump intensities, relatively high, above 60 W/cm^2 . The pump intensity dependent PL data were modelled within a simplified three-level erbium scheme [14]. It can be shown that the pump intensity dependence of the visible PL from erbium is given by [14]:

$$I_{\text{PL}} = \frac{I_{\text{PLmax}}}{1 + \frac{\tau^{-1}hc}{\sigma_{\text{ex}} p_{\text{ex}} \lambda_{\text{ex}}}} \quad (2)$$

where I_{PLmax} is the maximum PL intensity, h , the Plank's constant, c , the speed of light, p_{ex} , the pump power, and λ_{ex} is the excitation wavelength. Fitting the experimental data of Eq. (2), an estimate of the excitation cross-section σ_{ex} can be obtained. The fitting

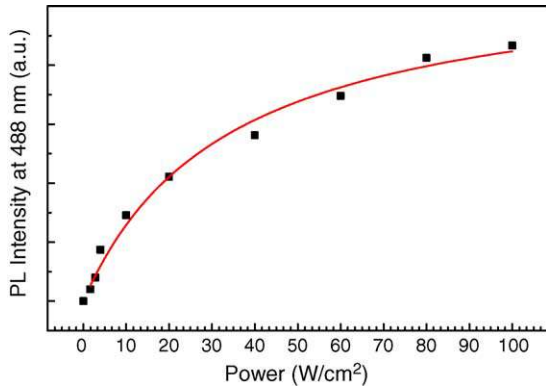


Fig. 5. Green PL intensity of erbium-doped PS as a function of a pump power. The solid line is the best fit from Eq. (2).

yielded $\sigma_{\text{ex}} = 1.2 \times 10^{-19} \text{ cm}^2$ with $\lambda_{\text{ex}} = 488 \text{ nm}$ and $\tau = 1 \text{ ms}$ being fixed parameters. This value for the σ_{ex} seems reasonable compared to the cross-section of erbium transition in other host materials [14]. In particular, σ_{ex} is nearly that of erbium ions in nc-Si implanted in SiO_2 . As it has been suggested by Kenyon et al. [15], the saturation of the PL intensity with pump power is due to the fact that the luminescence is limited by the availability of Er^{3+} in close proximity to silicon nanocrystals. Consequently, the optical cross-section increases compared to that in stoichiometric SiO_2 where the Er^{3+} PL intensity does not saturate (for the same Er^{3+} concentration in silicon nanocrystals) because the PL yield is not constrained by the availability of Er^{3+} ions but rather by the small absorption cross-section. Thus, it seems that most of Er^{3+} ions incorporated in PS from the electrochemical method is localized in c-Si nanocrystallites.

4. Conclusion

PS is doped with erbium ions by using the electrochemical deposition. A relatively uniform incorporation of erbium ions in the PS layer was evidenced from RBS and EDX analysis. In the presence of erbium, new well-defined luminescent centres are formed. The formation of these sites results in the creation of a defect-related level in the band gap at 0.206 eV below the conduction band. The weak temperature quenching of the erbium PL intensity is explained by both back transfer and Auger processes. Pump intensity dependent PL studies revealed that the excitation cross-section is the order of $1.2 \times 10^{-19} \text{ cm}^2$. The present results suggest that PS doped with erbium appears to be very attractive material for optical waveguide at $1.53 \mu\text{m}$.

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