Erbium-doped nanocrystalline silicon thin films produced by RF sputtering, annealing effect on the Er emission

M.F. Cerqueira¹, T. Monteiro², M. J. Soares³, A. Kozanecki³, P. Alpuim¹ and E. Alves⁴

¹Departamento de Física, Universidade do Minho, Braga, Portugal.
²Departamento de Física e I3N, Universidade de Aveiro, 3710-193 Aveiro, Portugal.
³Institute of Physics, PAS, Warsaw, Poland
⁴Instituto Tecnológico e Nuclear, EN 10, 2686-953 Sacavém, Portugal

Contact author: fcerqueira@fisica.uminho.pt

In the present work, erbium doped nanocrystalline silicon thin films were produced by reactive magnetron sputtering on glass substrates under different conditions (substrate temperature and Er content). The film structure was studied using Raman spectroscopy. The chemical composition was determined using the RBS technique. All the samples show sharp $^4I_{13/2} \rightarrow ^4I_{15/2}$ intra-$f$ emission of Er$^{3+}$ related centres with its maximum positioned at the 1.54 µm. However, the intensity of this transition (strongly dependent on the chemical composition of the matrix where the nanocrystals are embedded in and also on the structure of the matrix) changes after thermal annealing treatment. For the less crystalline samples our results show an increase of the Er$^{3+}$ PL intensity and for the highly crystalline ones the Er emission vanishes even at low temperature. This behavior was studied and explained in this work, on the basis of energy transfer between Si and Er ions.

1. Introduction
The achievement of efficient room-temperature light emission from Si is a crucial step toward the fully integrated Si-based optoelectronics. Erbium doped crystalline silicon (c-Si:Er) is a strong candidate for the fabrication of emitters and detectors to be used in optical telecommunication systems due to its intraionic luminescence line at 1.54 µm. However, the severe thermal quenching of the photoluminescence observed in c-Si:Er, makes the effectiveness of this system questionable [1]. The situation may be improved by the incorporation of Er ions in hydrogenated nanocrystalline silicon (nc-Si:Er) [2].
Nanocrystalline silicon thin films consist of small Si crystals embedded in an hydrogenated amorphous matrix (a-Si:H). The silicon nanocrystal size is typically in the range form 3 to 8 nm. Silicon nanocrystals (NCs) may act as the excitation species for Er ions, though the confinement of NCs in the amorphous Si matrix is hard to realize.

In this contribution we investigate thin films with this type of structure, studying Er-related PL dependence on the film structure, annealing and chemical composition of the matrix. Erbium-doped nanocrystalline silicon thin films were deposited by the reactive magnetron sputtering tech-nique, using a c-Si target covered with pieces of metallic Er. It is shown that it is possible to produce by this method Er-doped nc-Si:H thin films emitting at room temperature. The advantage of these films, compared to the more common SiO2 structures containing Si NCs is their relatively high electrical conductivity, which makes the material attractive for device applications.

2. Experimental

Erbium doped nanocrystalline silicon (nc-Si:Er) thin films were deposited by radio frequency (RF) plasma assisted reactive magnetron sputtering in an Ar/H2 atmosphere on ordinary glass substrates. Samples with different structural parameters (overall crystallinity, CR; crystal size, D, and matrix composition), were obtained by varying the deposition parameters. The fixed deposition parameters are the RF power (80W) and the hydrogen fraction defined as $\text{RH} = \frac{p_{\text{H}_2}}{(p_{\text{H}_2} + p_{\text{Ar}})} = 0.63$ where the $p_{\text{H}_2}$ and $p_{\text{Ar}}$ are the partial pressure of H2 and Ar respectively. The substrate temperature was 50ºC for Er34 sample, 150ºC for P13 sample and 300ºC for the others depositions. The target used was a c-Si of high purity (99.99%). The erbium was placed in a low erosion area on the silicon target, in order to keep the moderate rate of Er doping. The substrate-target distance was fixed at 55 mm. The chemical composition was determined by Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection (ERD) technique. The structural characterisation was done by micro-Raman spectroscopy under excitation with the 514.5 nm line of an Ar+ laser using a Jobin Yvon triple monochromator. With the 488 nm and 514.5 nm lines of an Ar+ laser as excitation sources, photoluminescence measurements in the infrared spectral region have been performed in the temperature range of 70-300 K using a Brucker 66V Fourier-transform spectrometer. The signal was
detected with a North-Coast EO-817 liquid nitrogen cooled germanium detector. The structural characterization as well as the erbium emission was evaluated prior and after the annealing treatment (400°C for 2h).

3. Results and discussion
The chemical composition was determined by combining the Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection (ERD) techniques (see Table 1). Some deposited films are characterized by low oxygen content and large hydrogen content (samples Er34, P13 and P17), whereas P25 sample has large oxygen content when compared with their hydrogen content.

The average nanocrystal size and the crystalline phase fraction, presented in Table 1, were estimated from the Raman spectra by fitting them in the framework of the Campbell-Fauchet model [3]. These structural parameters were confirmed using the standard procedure based on transmission electron microscopy (TEM) and X-ray diffraction studies as described in ref [4].

Table 1 – Atomic concentration and structural parameters: DR - average crystal size by Raman; CR- crystalline volume fraction by Raman; d- film thickness.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Er (at%)</th>
<th>Si (at%)</th>
<th>O (at%)</th>
<th>H (at%)</th>
<th>D_R (nm)</th>
<th>C_R (%)</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er34</td>
<td>0.03</td>
<td>72</td>
<td>&lt;4</td>
<td>28</td>
<td>&lt;3</td>
<td>34*</td>
<td>1900</td>
</tr>
<tr>
<td>P13</td>
<td>0.55</td>
<td>70</td>
<td>9</td>
<td>18</td>
<td>&lt;3</td>
<td>34*</td>
<td>760</td>
</tr>
<tr>
<td>P17</td>
<td>0.6</td>
<td>65</td>
<td>10</td>
<td>25</td>
<td>&gt;7</td>
<td>52</td>
<td>1260</td>
</tr>
<tr>
<td>P25</td>
<td>0.89</td>
<td>74</td>
<td>16</td>
<td>9</td>
<td>&gt;7</td>
<td>61</td>
<td>480</td>
</tr>
</tbody>
</table>

*estimated from TEM images

Figure 1 shows the Raman spectra of the as-deposited films. The presence of silicon nanocrystals is identified by the appearance of the TO vibrational mode characteristic of c-Si (approximately at 520 cm⁻¹). The presence of a-Si:H is confirmed by a broad band at around 480 cm⁻¹. It is seen that all the produced samples show the presence of a silicon amorphous phase. The crystalline volume fraction of the films (for the fixed RF power)
increases with the increase of the substrate temperature, from 34% to 61% at 50°C and 300°C, respectively.

Although samples grown at substrate temperature between 50°C and 150°C look like amorphous by Raman analysis, the Er34 sample, has been extensively characterized by transmission electron microscopy (TEM) (see ref [5]) shows a volume fraction of 34% of silicon nanocrystallites with a size < 3nm embedded in an a-Si:H matrix.

![Raman spectra](image)

Figure 1 – Raman spectra of studied films showing the amorphous and crystalline components. Inset shows the Raman spectra of the samples annealed at 400°C.

According to the Raman analysis, the as-grown erbium-doped silicon samples produced by RF sputtering can be separated into two groups, namely one group of samples having Si crystal sizes lower than 3 nm (Er34 and P13) and the other group having larger silicon crystals size (P17 and P25 samples). The estimated values, based on Raman spectra, of the crystalline volume fraction, CR, and of the crystallite size, DR, are given in Table 1.

With the aim of investigating how the different micro-structures (D, C and chemical matrix composition) influence the Er^{3+} photoluminescence (PL), the room temperature PL spectra of the as-grown samples are compared in Fig. 2. All the spectra are characterised by the presence of the 1.54 μm peak originated by interatomic $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} ions. The Er^{3+} luminescence is more intense for the samples having small sized Si nanocrystals (< 3 nm) than for those having larger sized NCs (> 7 nm), in agreement with other groups [6]. PL was excited off-resonance, so to have intense PL at room temperature two factors are necessary: efficient excitation and
reduced quenching. It is well known that Er in a-Si:H shows much less thermal quenching than Er in c-Si [7] and this is the most obvious explanation. However, since in all the samples there exist Si NCs, we can not exclude another mechanism, that means the Si size effect. Interestingly, the most intense Er$^{3+}$ PL peak are recorded for samples with quite different erbium content (Er34 having 0.03 at.% and P13 having 0.55 at.%). From these facts we can infer that (i) Er concentration of 0.03 at% is enough to obtaining the characteristic Er$^{3+}$ emission and (ii) 0.55 at.% is not in excess for getting the Er emission, this means that, in this concentration range, erbium does not form Er metallic clusters in the films or non emitting components...

![Graph showing PL intensity vs wave number for Er34 and P13 samples](image)

Figure 2 – Room temperature (RT) $^4 I_{13/2} \rightarrow ^4 I_{15/2}$ Er$^{3+}$ luminescence spectra obtained with the 514.5 nm laser line excitation for the as-deposited samples with low-crystalline fraction. Inset: RT PL for samples with high-crystalline fraction (P13 is for comparison)

Furthermore, since films Er34 and P13 (with D < 3 nm and low crystalline volume fraction) have very different hydrogen and oxygen content and show the highest Er$^{3+}$ PL intensity, we can infer that the matrix chemical composition is not the key factor controlling the Er$^{3+}$ emission. Moreover samples P17 and P25 show almost no Er$^{3+}$ PL having also very different chemical composition. We conclude that in a mixed phase material (a-Si:H and nc-Si) small Si nanocrystals are more favourable than large Si NCs to the energy transfer to the erbium ions. Indeed, this result is in agreement with Franzo et al [8] that have re-reported that for Si-rich material, the only crucial point is the presence
of a high density of small Si clusters that can act as both the absorbing medium and sensitizers for Er.

In order to clearly identify this crystal size effect on the excitation of Er ions, the films were thermal annealed in air for 2h at 400°C. Figure 3 depicts the room temperature photoluminescence spectra of the annealed samples showing the Er$^{3+}$ luminescence around 1.54μm. As obtained for the as-deposited samples, the low-crystalline fraction samples (Er34 and P13) show stronger Er$^{3+}$ luminescence than the samples with higher crystalline content (P17 and P25), for which the intraionic PL is nearly absent. Interesting are the results observed for the Er34 sample, with small sizes of the nanocrystals, which shows, again, the highest intensity.

The Raman spectra of the annealed films are similar to those obtained before annealing (Inset of Fig.1). Thus, the thermal annealing treatment had no effect on the sample structure, i.e. the 400°C annealing treatment did not induce sample crystallization. It is known that for a-Si:H thin films annealing at temperatures higher than 300-350°C induce the outdiffusion of hydrogen and consequent increase of structural disorder [9]. The hydrogen outdiffusion and the consequent increase of structural disorder are then expected for the annealed samples in the present work. However no changes in the FWHM values of the Raman peaks have been observed. Therefore neither crystallization nor increase of structural disorder did occur as a consequence of the annealing treatment. However the intensity of Er$^{3+}$ still increases for the low-crystalline samples and vanished for the high-crystalline ones, after annealing.

However, at this annealing temperature, it is possible that a partial atomic reordering occurs, not detected by Raman [10] possibly accompanied by the diffusion of light impurities in the Si-network. Since there was no observed hydrogen exodiffusion (no changes in the FWHM values of the Raman peaks), the effect of the annealing on the low-crystalline samples (having hydrogen content between 17 and 27 at.%) could be a reduction of the number of defects through passivation with hydrogen. Consequently a reduction of the number of non-radiative pathways for re-combination of electron-hole pairs occurs and so the Er$^{3+}$ PL increases. This process of network local reconstruction can also lead to the activation of the charge-transfer dopants since it is assisted by mobile light atoms (e.g. hydrogen or oxygen) in the Si network [11, 12]. For the high-crystalline
samples, the annealing effect was to decrease $\text{Er}^{3+}$ PL. It is known that hydrogen exodiffusion curves from nc-Si:H show a low-temperature peak at around 250ºC, a lower temperature the one observed for the corresponding peak in a-Si:H films [13]. Probably for the high CR samples with a large number of grain boundaries, the atomic hydrogen evolves from the silicon network, leaving behind many dangling bonds (DB) at the grain boundaries. These DB, will act as non-radiative recombination centres that will hinder energy transfer to the emitting centre.

![Graph showing PL intensity vs. Wavelength](image)

Figure 3 – Room temperature (RT) $^4I_{13/2} \rightarrow ^4I_{15/2}$ Er$^{3+}$ luminescence spectra obtained with the 488 nm laser line excitation for the annealed samples.

For the better understanding the annealing effect, low temperature PL measurements of the annealed samples were performed. Figure 4 shows the PL spectra recorded at 70K, for the emitting samples. Once again, only the samples with lower crystalline fraction reveal intraionic PL. Even when the temperature is cold down the Er$^{3+}$ PL is absent for the highest crystalline samples, although they have erbium content higher than 0.03 at% and the hydrogen content although lower than for Er34 sample is still high (25 at% for P17 and 9 at.% for P25 sample) meaning that the energy transfer becomes even less efficient after annealing for these samples.

For samples with the lower crystalline fraction (Er34 and P13) the Er$^{3+}$ PL intensity at RT is nearly 50% of its initial value at 70 K for both samples which suggests similar extinction processes.
Figure 4 – 70K \(^{4}I_{13/2} \rightarrow ^{4}I_{15/2}\) Er\(^{3+}\) luminescence spectra obtained with the 488 nm laser line excitation for the annealed samples.

A more accurate analysis was performed for sample Er34 as shown in Figure 5. Between 70 K and 180 K the Er\(^{3+}\) integrated intensity is well accounted for by a thermal population described by an activation energy of 5 meV, followed, for higher temperatures of non-radiative de-excitation processes that can be well fitted to an activation energy of 200 meV. The Er34 sample presents the highest PL intensity. As both the Er34 and P13 samples do not differ in microstructure but in matrix chemical composition (sample Er34 having much more hydrogen than P13), we suggest that its much higher PL intensity could be determined by the chemical composition of the Si matrix.

Figure 5 – Temperature dependence of the \(^{4}I_{13/2} \rightarrow ^{4}I_{15/2}\) Er\(^{3+}\) luminescence spectra obtained with the 488 nm laser line excitation for the Er34 sample. Inset: Evolution of the integrated PL intensity with temperature.
4. Conclusions
Er-doped nc-Si:Er:H films were deposited by co-sputtering. After deposition the films were annealed and investigated through Raman spectroscopy and PL measurements. According to the experimental results, annealing at 400ºC does not cause important structural changes. However, a considerable change on the Er-related PL intensity at 1540 nm was verified: an enhancement of the PL for the less crystalline films and a suppression of the PL for the highly crystalline films. From the results of the present work, it can be conclude that in the case of mixed phase (amorphous matrix with Si NCs embedded in): (i) there exist a higher excitation efficiency of Er ions for samples having small nanocrystals than bigger ones; (ii) the enhancement of the luminescence efficiency, after annealing, in the less crystalline samples seems to be deter-mined by chemical aspects of the Si matrix, mainly hydrogen content; (iii) the practically vanished Er3+ luminescence for the highly crystalline samples suggest that it is consequence of the reduced excitation efficiency of Er ions due to the presence of a large number of big crystals.

5. References