

## Effect of the matrix on the 1.5 $\mu\text{m}$ photoluminescence of Er-doped silicon quantum dots

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**Abstract:** Erbium doped nanocrystalline silicon thin films were produced by reactive magnetron r.f. sputtering. Their structural and chemical properties were studied by micro-Raman, spectroscopic ellipsometry and Rutherford backscattering spectroscopy. Films with different crystalline fraction and crystallite size were deposited by changing the deposition parameters. The impact of the composition and structure of Erbium ions environment on the 1.5  $\mu\text{m}$  photoluminescence is discussed.

### 1. Introduction

The achievement of an efficient room-temperature light emission from Si is a crucial step toward the fully integrated Si-based optoelectronics. Er-doped silicon takes special significance for optical communication systems due to the emission line at 1.54  $\mu\text{m}$ , originated by inter-atomic  $^4I_{13/2} \rightarrow ^4I_{15/2}$ . However, Er-doped bulk crystalline silicon, c-Si:Er, operating under forward bias still present unsolved problems such as the strong temperature quenching of Er emission [1]. The situation may be considerably improved by the incorporation of Er ions in nanocrystalline silicon. This idea is based on the band-gap widening of nanometer sized Si, which results in a reduction of the thermal quenching of Er luminescence.

Intrinsic nanocrystalline silicon (nc-Si) and Er-doped nanocrystalline silicon have been attracting enormous interest of researchers as promising candidates for the realization of Si-based visible and infrared light emitters [2]. Indeed, evidences have been reported that Er-doped nc-Si thin films have enhanced intra-ionic luminescence and reduced thermal quenching with respect to the crystalline Si [3-6]. Moreover, controversial results have been obtained for the Er related radiative lifetime and quenching mechanisms, as pointed in ref [7]. In this work, we study the nanostructure of Er-doped nc-Si thin films deposited by reactive magnetron sputtering and we discuss the effect of hydrogen and oxygen incorporated into films on their photoluminescence properties.

## 2. Experimental

Erbium doped nanocrystalline silicon (nc-Si:Er) thin films were grown by r.f. reactive magnetron sputtering in Ar/H<sub>2</sub> atmosphere using a procedure similar to that applied for the preparation of undoped  $\mu$ c-Si:H films [8], and adding small pieces of metallic erbium, outside the erosion area, to the c-Si target. We grew two groups of samples that differ by the amount of oxygen and hydrogen incorporated into the films. For each group, samples with different structure were deposited by varying the deposition temperature. In particular, we grew samples with the oxygen amount less than 2.5% (Er33 and Er34), and samples with an oxygen content of 5% (Er16 and Er17). The samples and the growth conditions are presented in Table 1.

The chemical composition (see Table 1) was determined by combining Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection technique (ERD). For the structural characterisation, we used micro-Raman spectroscopy under excitation with 514.5 nm line of Ar<sup>+</sup> laser. Spectroscopic ellipsometry (SE) was also applied to analyse the film structure along the growth direction. These spectra were analysed using models based on the Bruggeman effective medium approximation BEMA [9]. PL measurements in the infrared spectral region were performed with the Bruker 66V Fourier-transform spectrometer. The signal was detected by North-Coast germanium detector, model EO-817, being excited by the 514.5 nm line of an Ar<sup>+</sup> laser. The samples were placed on the cold finger of a continuous-flow liquid He cryostat and studied in the temperature range between 6K and RT.

Table 1: Growth conditions for Erbium doped nanocrystalline silicon thin films and respective atomic concentration and structural parameters

Sample	Temperature (°C)	RF power (W)	Er (%)	Si (%)	O (%)	H (%)	D <sub>TEM</sub> (nm)	D <sub>R</sub> (nm)	C <sub>R</sub> (%)
Er33	25	80	0.02	73.4	<1	25.8	3	-	-
Er34	50	80	0.03	72.3	0	27.5		-	-
Er17	400	80	0.06	79	5	16		7.8	73
Er16	250	80	0.07	76	5	19		7.3	64

D - Average crystal size by Raman; C<sub>R</sub>- crystalline volume fraction by Raman

### 3. Results and discussion

#### 3.1 Structural and chemical characterisation

Figure 1a) shows the Raman spectra for some representative nc-Si:Er samples. The broad band (at around 480 cm<sup>-1</sup>) observed in the spectra is related to the silicon amorphous matrix and is present for all samples. The nanocrystalline samples show a narrow peak in the vicinity of 521 cm<sup>-1</sup> related with the presence of crystallites. This peak is generally attributed to the transverse optical mode (TO) of crystalline silicon and is shifted to smaller wave numbers for decreasing crystal diameter due to the spatial confinement of phonons. It is found that the first group of samples, grown at low deposition temperature, does not show any crystalline peak in the Raman spectra. These samples have very low oxygen content (the ratio O/H is less than 0.05). In contrast, the crystalline peak is seen for the other samples (Er17 and Er16 samples), which were deposited at higher temperature and have about 5% of oxygen. To analyze the Raman spectra, computer simulations were used, considering the spectral profile as a superposition of the amorphous and crystalline parts. The crystalline profile was calculated based on the Strong Phonon Confinement [10] and a Gaussian profile was attributed to the amorphous TO peak. The structural and compositional results are presented in Table 1.

Analysing the obtained structural parameters and the growth conditions it comes out that for the fixed r.f. power of 80 W, the increase of the deposition temperature promotes the formation of larger silicon crystallites, since the substrate temperature provides energy to the sputtered atoms for finding in the solid the equilibrium position (crystalline form) in solid. Furthermore, the amount of crystalline fraction also increases from a very low fraction (case of Er33 sample) until almost 80% (Er17 sample). However, Raman spectra are not sensitive

to very small crystallites with the sizes  $<5\text{nm}$ , since below this typical dimension the broadening and shift of the crystalline TO mode is so high that it merges into the amorphous peak. Therefore, a deeper insight into the films structure was obtained by spectroscopic ellipsometry. The best-fit BEMA models from which the structure is derived show a very complex layered structure of the films due to the oxygen in-diffusion profile [11].

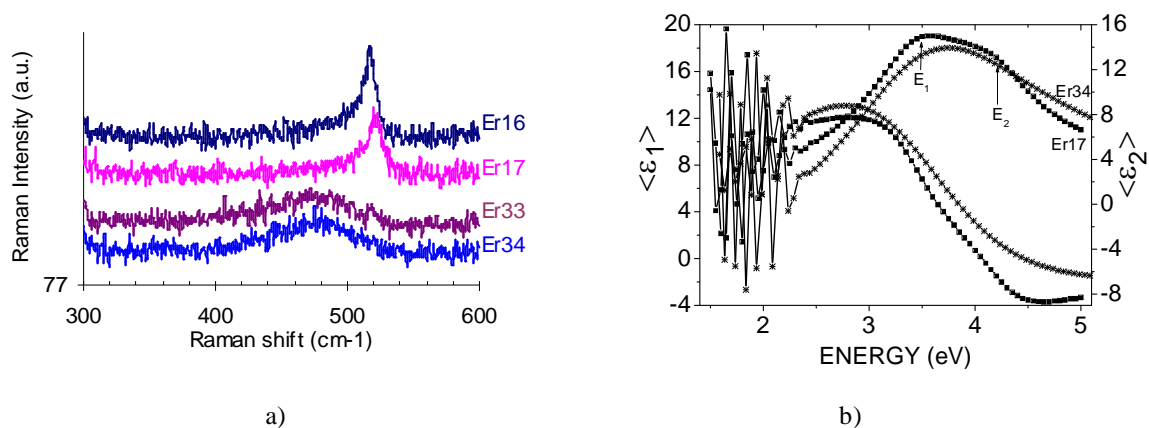


Figure 1: a) Raman spectra of the examined samples with different crystallinity. b) Typical SE spectra of the real,  $\langle \epsilon_1 \rangle$ , and imaginary,  $\langle \epsilon_2 \rangle$ , parts of the pseudodielectric function obtained for the Er17 and Er34 samples.

Figure 1b) shows the ellipsometric spectra of the real,  $\langle \epsilon_1 \rangle$ , and imaginary,  $\langle \epsilon_2 \rangle$  parts of the pseudodielectric function of some representative films with (Er17) and without (Er34) oxygen incorporated into the matrix. The observed different pseudodielectric response is related with the differences in samples nanostructure. In particular, the SE spectra of the Er17, and Er16 samples (with 5%O) show pronounced  $E_1$  and  $E_2$  critical points (CPs) at approximately 3.4 eV and 4.2 eV that are distinctive interband transitions of c-Si. The presence of the CPs indicates a large crystalline fraction. In contrast, the SE spectra of the Er33 and Er34 samples (with  $0\% < 2.5\%$ ) shows the  $\langle \epsilon_2 \rangle$  spectra with a single peak at about 3.6 eV that is a characteristic of the hydrogenated amorphous silicon (a-Si:H). The SE spectra are consistent with the Raman spectra. Nevertheless, the SE spectra of these samples have indicated that the optical gap of these films exceeds 2eV. This high-gap value could not be explained either by the large content of hydrogen into the a-Si network (for a 27% of hydrogen in a-Si we found an optical gap of 1.87 eV), nor by the presence of SiO because of the very low oxygen content. The best-fit of SE spectra was obtained

only by including in the film structure a volume fraction of 25% of small Si nanocrystals with the diameter of 1-3 nm embedded in the a-Si:H tissue. The presence of these nc-Si has been also confirmed by the TEM analysis [12]. These samples have very low oxygen content, and a large amount of hydrogen as determined by RBS. Therefore, it is reasonable to suppose that the oxygen is active ionizing the erbium, while hydrogen is essential for the passivation of crystallite grain boundaries and dangling bonds in the amorphous matrix where crystallites are embedded in. The corresponding best-fit models that depict the film nanostructure are shown in figure 2 for the representative Er34 and Er17 samples. The difference between the two groups of samples is not only the crystallites size but also the matrix, in which the crystallites are embedded. For the first series of samples (with the very low oxygen content) the silicon crystallites are embedded in a hydrogenated amorphous a-Si:H matrix. For the other ones (with higher oxygen content) the crystallites of larger diameters are embedded in the matrix that is represented by the mixture of hydrogenated amorphous silicon (a-Si:H) and silicon oxide (SiO). Furthermore, while the nc-Si/a-Si:H structure is quite homogeneous along the film thickness, the oxygen containing samples present a layered structure, where the various layers differ by their SiO content. In particular, segregation of oxygen towards the outmost layer is found (which can be explained by the oxygen diffusion profile), and the larger the crystalline volume fraction, the lower the SiO volume fraction.

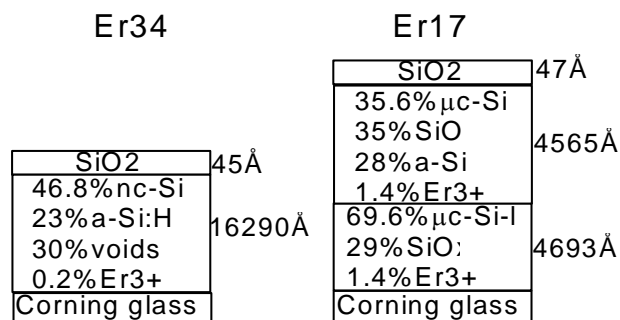


Figure 2: Best-fit models of SE spectra showing the layered structure of the representative Er34 and Er17 samples. Here nc-Si marks the crystalline phase with the average size of crystallites <3nm; μc-Si – the crystalline silicon phase with the average size of crystallites >6nm.

It is well known that for the growth of good quality amorphous silicon thin films the hydrogen is essential to improve their optical and electrical quality, since the hydrogen will bond to the silicon in order to saturate the silicon dangling bonds (DB). Similarly, the main role of the large hydrogen content in the first group of samples consists in the saturation of the DB in the amorphous matrix and on the crystallites grain boundaries. For the group of samples with a large crystalline fraction and larger crystallites, oxygen also participates in the grain boundaries passivation, forming SiO bonds.

The peculiarity of the SE analysis is in highlighting the interrelation between composition/microstructure and optical properties. In particular, the obtained data for the nanostructure and composition of matrix can be used to explain the photoluminescence properties of the erbium-doped films.

### *3.2 Photoluminescence study*

The Er related photoluminescence (PL) spectra obtained at 6K for some nc-Si:Er samples are shown in figure 3. For all of these samples one can see the characteristic peak with maximum around 1.535  $\mu\text{m}$ , that is attributed to the Er related centers.  $\text{Er}^{3+}$  ions could be incorporated both in the Si nanocrystals and in the surrounding amorphous matrix. It is well known that the excitation cross section of  $\text{Er}^{3+}$  ions in crystalline Si is in about 7 orders of magnitude higher, than in amorphous materials [13], therefore with the increasing of the films crystallinity we would expect the increase of Er PL behaviour. On the other hand, the sensitization effect of  $\text{Er}^{3+}$  by nanocrystals should be less pronounced in the structures with the large crystallites. The latter is related with the decreasing of the band gap energy for large sizes that at some point will not match with the energy of  $\text{Er}^{3+}$  intracenter transitions.

The PL data presented indicate that the PL intensity is noticeable higher for samples with very small nanocrystals (size < 3nm) embedded in a well passivated a-Si:H matrix in comparison with the samples containing larger crystallites embedded in a mixed a-Si:H/SiO matrix. The lower PL intensity for the second group of samples could be related with the increase of non-radiative pathways in the more disordered and non-homogeneous matrix.

Furthermore, it stays, that within the same group of samples (i.e., same composition of the surrounding matrix) the PL intensity increases with the volume fraction of the crystalline phase (e.g. Er34 vs Er33 and Er17 vs Er16).

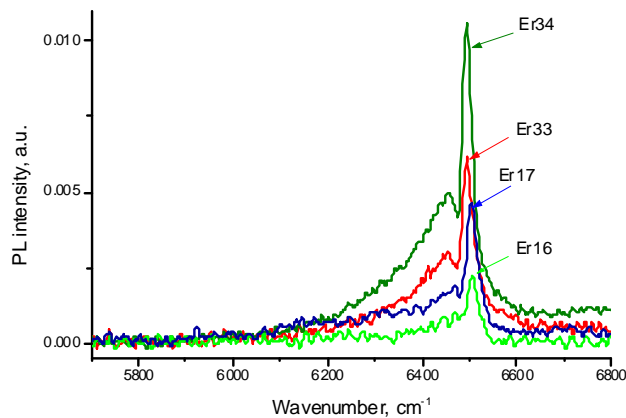


Figure 3: Low temperature infrared photoluminescence spectra for some typical nc-Si:Er samples being excited by the 514.5 nm line of an Ar<sup>+</sup> laser and 200mW of excitation power.

#### 4. Conclusions

Thin films of erbium-doped nanocrystalline silicon were prepared by reactive magnetron sputtering and their structural, chemical and optical properties were studied. We have studied the crystallinity/size dependence of the PL spectra. For samples with the same Er content, we observed the different intensities of PL peak assigned to the intra-4f transition of Er<sup>3+</sup> ions. It is found that the 1.54  $\mu\text{m}$  Er-related PL reduces strongly with the increase of silicon crystallite sizes and in the case when the crystallites are embedded in mixed a-Si:H/SiO matrix. The latter is probably related with the high structural disorder introducing non-radiative decay pathways. For samples, with the same crystallite size and matrix, the PL intensity increases with the increase of crystalline fraction.

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