

Interrelation between microstructure and optical properties of erbium-doped nanocrystalline thin films

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Abstract

Nanocrystalline silicon thin films codoped with erbium, oxygen and hydrogen have been deposited by co-sputtering of Er and Si. Films with different crystallinity, crystallite size and oxygen content have been obtained in order to investigate the effect of the microstructure on the photoluminescence properties. The correlation between the optical properties and microstructural parameters of the films is investigated by spectroscopic ellipsometry. PL response of the discussed structures covers both the visible wavelength range (a crystallite size-dependent photoluminescence detected for 5–6 nm sized nanocrystals embedded in a SiO₂ matrix) and near IR range at 1:54 μm (Er-related PL dominating in the films with 1–3 nm sized Si nanocrystals embedded in a-Si:H). It is demonstrated that the different PL properties can be also discriminated on the basis of ellipsometric spectra.

Keywords: nc-Si; Erbium doping; Spectroscopic ellipsometry; Optical properties; Films

1. Introduction

Efficient light emission at room temperature from silicon-based materials for optoelectronic integration is one of the main issues in current material research. A large amount of work has been reported on the emission of visible light from silicon nanocrystals [1,2]. Introduction of Er³⁺ ions into a Si network is a very promising approach to get light emission at 1:54 μm (that originates by the intra-4f transitions of Er³⁺ ions) [3]. Indeed, up to now materials that have been largely investigated are SiO₂:Er, a-Si:H, O, Er and c-Si:Er, the last one affected by a strong thermal quenching of the Er photoluminescence (PL). Recently, nc-Si:Er and μc-Si:Er have been investigated because it is thought that the band-gap widening of nanometer size Si could reduce the thermal quenching of PL. On the other hand, Si nanocrystals, that are well known to emit in the visible range, due to the recombination of confined excitons within the nanostructure, may act as efficient sensitizers for the erbium ions [4,5]. In the present contribution, the influence of the complex film nanostructure, i.e. the crystallites volume fraction and size, and the doping content (mainly erbium, hydrogen and oxygen), on the photoluminescence properties of the Er³⁺ ions and of Si-nanocrystallites is investigated. The peculiarity of this study is the use of spectroscopic ellipsometry (SE) to elucidate any correlation between the PL efficiency and the matrix. The films of nanocrystalline (nc)- and microcrystalline (μc)-Si:Er:H:O have been obtained by co-sputtering of Si and Er in an hydrogen rich atmosphere.

2. Experimental

Erbium-doped nanocrystalline silicon thin films were grown by reactive magnetron sputtering on ordinary glass substrates. The target was a c-Si wafer where some pieces of high purity (99.99%) metallic erbium were added for the Er doping. The RF power was kept constant and equal to 80 W during all the experiments. All the samples were grown in a hydrogen-rich atmosphere, $R_H = 0.63$ ($R_H = p_{H_2}/(p_{H_2} + p_{Ar})$ is the hydrogen fraction); oxygen was present at a contamination level during deposition. Substrate temperature was varied in the range 25–400°C in order to have films with different nanocrystalline size and volume fraction [6].

Compositional data, i.e., the Si, H, O, and Er atomic percentage, were obtained by Rutherford backscattering (RBS) analysis. The atomic percentage of Er in the analyzed films was estimated by RBS to be in the range 0.02–0.2%.

Structural characterization of the size and volume fraction of crystallites was carried out by X-ray diffraction (XRD), Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM) and spectroscopic ellipsometry (SE). SE spectra of the real, $\langle \epsilon_1 \rangle$, and imaginary, $\langle \epsilon_2 \rangle$, parts of the complex pseudodielectric function, $\langle \epsilon \rangle = \langle \epsilon_1 \rangle + i \langle \epsilon_2 \rangle = (n + ik)^2$ (n is the refractive index and k is the extinction coefficient) were measured in the 1.5–5.5 eV energy range by using a phase-modulated spectroscopic ellipsometer (UVISEL-Jobin Yvon) at an incidence angle of 70.57°.

Since spectroscopic ellipsometry distinguishes the optical constants, namely the refractive index and extinction coefficient, of stoichiometric, SiO₂, and substoichiometric, SiO, silicon oxides, it was found that in the present films silicon crystallites are embedded in complex SiO or a-Si:H matrix.

PL measurements in infrared spectral region have been performed with a Bruker 66V Fourier-transform spectrometer. The signal was detected with a North-Coast EO-817 liquid nitrogen cooled germanium detector. The 514.5 nm line of an Ar laser was used for the excitation. The samples were placed on a cold finger of a continuous-flow liquid He cryostat in vacuum being studied between 6 K and RT. In the visible range, photoluminescence spectra were recorded using a Spex Fluorolog spectrometer (1680-B monochromators with a dispersion of 1.70 nm/mm) equipped with a R943 Hamamatsu photomultiplier. The spectra presented were obtained under samples excitation at the wavelength of 350 nm from the continuum Xenon lamp spectrum (output power ~ 2 mW, and a spot area ~ 10 mm²).

3. Results and discussion

Fig. 1 shows the SE spectra of the imaginary part, $\langle \epsilon_2 \rangle$, of the pseudodielectric function of various erbium-doped silicon films with different crystallinity and crystallite size, as also determined by XRD and Raman data (reported in Table 1). It can be seen that the films can be grouped in three categories depending on SE spectra and their crystalline volume fraction. It is worth mentioning that these three categories of films have different PL properties, as can be deduced from the PL data in Fig. 2. In particular, films with very high SE spectra and well pronounced E_1 and E_2 critical points, that are interband transitions characteristics of c-Si (the E_1 transition takes place along the Λ directions of the Brillouin zone, and E_2 represents higher transitions involving the second lowest conduction bands of c-Si) [7] have a crystalline fraction higher than 65% and a crystallite size larger than 8 nm do not show any visible or infrared PL, although it shows the presence of Er³⁺. This is because in these highly microcrystalline samples with very large grains, grain boundary defects are not well passivated by hydrogen or oxygen (see the very low H% and O% in Table 1). Hence, they are not able to emit light in the visible range or to transfer energy to Er³⁺ ions, because of their very low band gap (<1.2 eV),

which makes it difficult to activate the Er^{3+} transition, and large density of grain boundaries that result in a non-radiative decay.

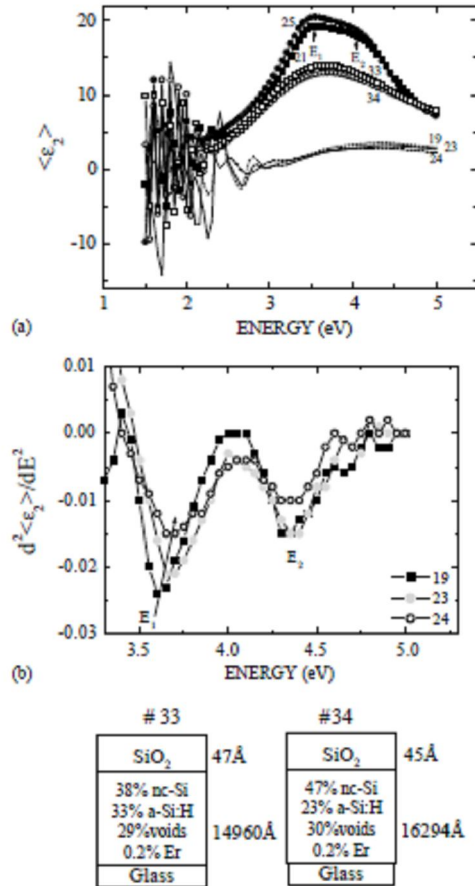


Fig. 1. (a) SE spectra of the imaginary part, $\langle \epsilon_2 \rangle$, of the pseudodielectric function of erbium-doped silicon thin films with different crystallite size and volume fraction; (b) detail of the second derivative spectra of samples 19, 23, 24 of (a) in the region 3.2–5.0 eV. The best-fit models of SE spectra of Er33 and Er34 that include nanocrystals not detected by Raman (see Table 1) are also shown at the bottom.

Another category of films is characterized by very low SE spectra that seems to be featureless and whose interference system extends to about 3 eV providing evidence of a large band-gap value. Nevertheless, the second derivative spectra shown in Fig. 1b put in evidence the presence of E_1 and E_2 peaks that are indicative of the presence of crystallites, as also corroborated by Raman data summarized in Table 1. From the fit analysis of the SE spectra, we derived that these films consist of an SiO tissue with an optical band gap of about 3 eV where a fraction (<40%) of crystallites are embedded. The peculiarity of these erbium-doped films is the PL emission in the visible range as shown in Fig. 2. The PL spectra of these samples are very broad and many peaks can be seen at different energy values. In particular, all samples, Er19, Er23 and Er24, exhibit a PL broad peak at around 1.77 eV, which has been already observed by others [8] in PL spectra of as-deposited SiOx films with various oxygen content. Furthermore, sample #23 has an additional PL peak at higher energy of 1.99 eV, and for sample #24, with an average crystallite size <5 nm, a further peak at 2.04

eV appears. These high-energy PL peaks cannot be explained on the basis of the average crystallite size determined by Raman and XRD. Indeed, additional information on nanocrystals size is deduced by the position and broadening of E_1 peak in the SE spectra. In fact, on the basis of a well-consolidated correlation between the E_1 peak position and broadening and Si grain size [9], the presence of nanocrystallites with an average size lower than 3 nm (that cannot be seen by conventional Raman and XRD) can be inferred. Furthermore, the blueshift of the E_1 peak (see Fig. 1b) indicates that the average nanocrystallite size decreases in the order #19 > #23 > #24. Therefore, combined SE and Raman analysis gives a more complete size distribution and allow us to explain the PL spectra. In particular, the smaller (<3 nm) nanocrystallites are responsible of the PL peak at 2.04, 1.99 and 1.86 eV. Therefore, on the basis of PL peak energy position, a simple band-to-band recombination mechanism within the Si nanocrystallite cannot be ruled out. Indeed, SiO defect centers are also likely to be responsible for the high-energy PL of these films [8]. As an example, PL peaks due to a non-bridging oxygen-hole center [10] and Si_6 clusters [11] at 1.9 and 1.8 eV, respectively, that blueshift with increasing oxygen content have been reported in a-Si:O.

Table 1
Average crystallite size and volume fraction determined by Raman spectroscopy and RBS compositional data for some representative erbium-doped nanocrystalline silicon films

	Sample number						
	Er25	Er21	Er33 ^a	Er34 ^a	Er19 ^a	Er23 ^a	Er24 ^a
Size (Å)	83	79	Amorphous (from XRD and Raman)		65	60	50
Crystallinity (%)	70	65			40	33	23
Er (%)	0.1	0.1	0.02	0.03	0.12	0.1	0.2
H (%)	—	16.7	25.8	27.5	23	—	25.4
O (%)	—	8.8	< 1	0	34	—	17.6

^aIn these samples, crystallites with an average size < 3 nm have been detected by spectroscopic ellipsometry and HRTEM as indicated in the text.

The presence of visible luminescence in these samples explains the absence of Er^{3+} luminescence as the two processes of radiative decay of nanocrystals and Er^{3+} excitation are in competition with one another [12].

Another category of deposited films is characterized by $\langle \epsilon_2 \rangle$ SE spectra with a peak at about 3.6 eV and the extension of the interference system to energy values higher than 2 eV. Both XRD and Raman spectra were featureless indicating their main amorphous tissue. Nevertheless, the fit analysis of these SE spectra using the Tauc-Lorentz equation yields a band-gap value of about 2 eV, which is not characteristic of even largely hydrogenated ($H \sim 28\%$) a-Si. An HRTEM image of these samples is shown in Fig. 3 providing evidence of nanocrystallites whose size distribution is also reported in Fig. 3, being in the range of 1–3 nm. This nanometer size crystallites well explain the band-gap value found by SE spectra, as expected by quantum confinement effects. The peculiarity of these samples is the presence of the Er^{3+} ions PL at 1:54 μm , as shown in Fig. 2b. It is worth mentioning that these samples have been prepared by co-sputtering at room temperature in a H_2 rich atmosphere and show very low O amount (<1% from RBS) and a large H content ($\sim 28\%$), hence, the nanocrystals are embedded in an a-Si:H tissue and not in stoichiometric (SiO_2) or sub-stoichiometric (SiO) silicon oxides, as derived by the best-fit SE models in Fig. 1. Therefore, it seems that any role of the Si/SiO interface on the Er^{3+} PL activation can be ruled out. Furthermore, Er-doped a-Si:H films prepared in similar conditions do not show any PL at 1:54 μm ; hence, in the present case, Er^{3+} ions activation is not provided by the a-Si:H host. Rather, the very small nanocrystals play the main role in the Er^{3+} activation. In fact, it is

found (see SE models in Fig. 1) that the higher the nanocrystallite volume fraction, the higher the Er^{3+} PL intensity. Further PL investigations are in progress to clarify better the role of nanocrystals as Er sensitizers.

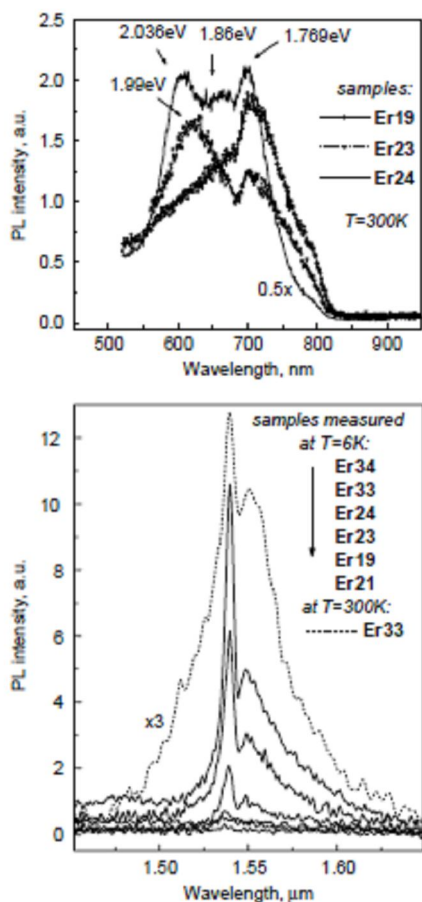


Fig. 2. (a) PL spectra in the visible range at $T = 300$ K for the samples 19, 23 and 24 shown in Fig. 1; (b) PL spectra in the infrared range at $T = 6$ and 300 K for some nc-Si samples. PL intensity in the infrared range decreases for the samples measured from the sample Er34 down to Er21. For the clearness, the PL curve obtained at 300 K for the sample Er33 is magnified by factor 3.

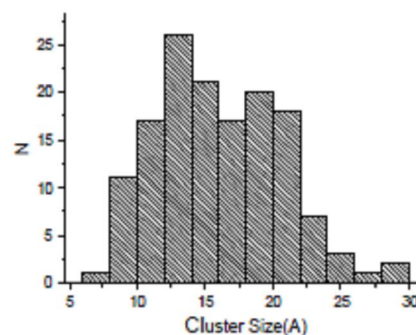
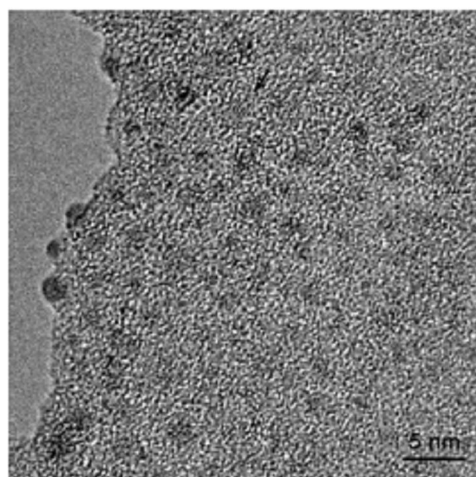


Fig. 3. HRTEM image of sample 33 of Fig. 1 showing the presence of silicon crystallites (001) oriented in the a-Si:H matrix. The crystallite size distribution is also shown.

4. Conclusions

Er-doped nanocrystalline thin silicon films with different crystallite size and volume fraction embedded in a-Si:H and SiO matrix have been prepared by c-Si and metallic erbium co-sputtering in H_2 rich atmosphere. Non-destructive optical characterization of nanostructure has been carried out by spectroscopic ellipsometry and corroborated by conventional XRD, Raman and HRTEM techniques. It is found that ellipsometric spectra (SE) can be used to predict and/or discriminate the photoluminescence properties of nc- and μc -Si:Er, O thin films. In particular, films with a crystalline volume fraction $>50\%$ and large crystallites (<6 nm), which can be recognized by very high SE spectra

with well pronounced E1 and E2 critical points, do not show any PL and Erbium-doped silicon films that have very low and almost featureless SE spectra corresponding to crystallites 6 nm embedded in a SiO₂ matrix show visible PL in the range 1.7–2.1 eV and finally, the Er³⁺ PL at 1.54 μm is observed in samples containing nanocrystallite with a size in the range 1–3 nm embedded in an a-Si:H matrix; these films can be recognized by SE spectra with a peak at about 3.6 eV and an optical band gap larger than 2 eV. The advantages of the SE analysis with respect to the conventional structural technique are that it is non-destructive, in contrast to HRTEM, and possible crystallization that can be induced during Raman/XRD measurements is avoided.

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