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Spectroscopic ellipsometry study of the layer structure and impurity content in Er-doped nanocrystalline silicon thin films

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Abstract

Er doped nc-Si thin films have been investigated by spectroscopic ellipsometry (SE). The optical response of Er ions in a nc-Si/SiO matrix has been determined by SE, and it has been used to detect Er contents as low as ≈0.2 at%. The complex layered nanostructure of nc-Si:Er:O has been resolved and it has been found that it is strongly influenced by the Er-doping and the oxygen in-depth distribution profile. SE results are discussed in comparison with data obtained by the standard methods of the X-ray diffraction, Rutherford backscattering and Raman spectroscopy.

Keywords: Spectroscopic ellipsometry; Nanocrystalline silicon; Erbium

1. Introduction

Erbium doped nanocrystalline silicon, nc-Si:Er, thin films produced by RF magnetron sputtering have been reported to be effective emitters at the 1.54 μm wavelength (corresponding to the intra-4f transition of Er^{3+} ions) in a wide temperature range from 5 to 300K [1]. Hence, they are attractive for applications in Sibased optoelectronic devices. However, the Er luminescence intensity in nc-Si thin films is strongly influenced by the complex nanostructure of films, i.e. the nanocrystalline volume fraction and crystallite size, and by the impurity content (mainly oxygen). Hence, it is important a detailed investigation of the ‘‘anatomy’’ of the nc-Si:Er,O films, i.e., the layered structure, the nonhomogeneous distribution of the nc-Si and a-Si phases, and the in-depth distribution of the SiO phase, which are strongly dependent on the growth conditions.

In this contribution, the nanostructure of nc-Si:Er,O thin films deposited by the RF magnetron sputtering is analyzed by spectroscopic ellipsometry (SE). By the SE technique, the optical response of Er ions in a nc-Si/SiO matrix has been determined and used to evaluate Er contents as low as 0.2 at% in the layers. Additionally, SE analysis reveals the complex layered structure and impurity distribution

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in nc-Si:Er,O films, whose optical response is described by the Bruggeman effective medium approximation (BEMA). In contrast, data obtained by X-ray diffraction and Raman spectroscopy only provide the average value of the crystallinity over the whole film thickness. The effect of the Er content on the structure of nc-Si thin film is discussed.

2. Experimental

Erbium doped nanocrystalline silicon thin films were grown on glass substrates by the reactive magnetron sputtering in H_2/Ar atmospheres with various H_2 percentages. The target was a c-Si wafer where some pieces of high purity (99.99%) metallic erbium were added for the doping. Growth parameters, such as the temperature, T_{gr}; the RF power, and the type of atmosphere (hydrogen or argon rich) were varied to obtain films with different Er-, H- and O-content and different crystallinity and nanocrystal grain sizes, as shown in Table 1.

Table 1
Growth conditions and sample parameters for undoped (Si#) and Er-doped (Er#) nc-Si films[a]

Sample	T_{gr} (°C)	RH	RF (W)	d (nm)	Er (%)	O (%)	Si (%)	D_x (Å)	ε_x (%)	D_R (Å)	c_R (%)
Si13	250	0.63	80	581	0	7	72	96	0.12	71	53
Si12	350	0.63	80	511	0	5	80	64	0.2	71	66
Er13	250	0.63	80	742	0.2	12	88	48	0.02	73	75
Er12	350	0.63	80	901	0.2	5	95	48	0.13	78	67
Er3	100	0.17	40	786	4.7	16.3	78	Basically amorphous			

[a] Here T_{gr} is the growth temperature; RH determines the hydrogen fraction in growth atmosphere derived from the ratio of partial pressures $RH = pH_2/(pH_2 + pAr)$; RF is the RF magnetron power; d is the thickness of the films, determined from the transmission spectra in UV-visible range; Er, O, and Si are elements content obtained by RBS method; D_x and ε_x are nc size and strain, determined by XRD method, D_R and c_R are the grain size and crystallinity of the films measured by Raman spectroscopy.

Spectroscopic ellipsometry measurements of the complex pseudodielectric function $\langle\varepsilon\rangle = \langle\varepsilon_1\rangle + i\langle\varepsilon_2\rangle$ of the films were performed in the range 1.5–5.5 eV. SE measured the energy dependence of the ellipsometric angles Ψ and Λ; and, hence, of the ratio, ρ; between the complex reflectance coefficients of two components of the polarized light, r_p; and r_s; respectively, parallel and perpendicular to the plane of incidence, according to the equation:

$$\rho = r_p / r_s = \tan\Psi \exp(i\Lambda), \quad (1)$$

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where Ψ is the amplitude ratio ($\tan\Psi = |r_p| / |r_s|$), and Λ is the phase difference ($\Lambda = \delta_p - \delta_s$) between the p and s components. The pseudodielectric function $<\varepsilon_2>$; was derived from the r parameter through the following equation [2]:

$$<\varepsilon>=\varepsilon_o \sin^2\phi_o\left[1+\tan^2\phi_o \frac{(1-\rho)^2}{(1+\rho)^2}\right], \quad (2)$$

where ϕ_0 is the angle of incident light and ε_o is the ambient dielectric function.

SE spectra were analyzed in terms of optical models based on the Bruggeman effective medium approximation (BEMA) [3] applying the least-squares regression method for the fitting, where the fit goodness was estimated by the parameter χ^2 [4]. The 95% confidence limit of fit parameters was also evaluated. The dielectric function of a-Si, nc-Si-fine grains, nc-Si-large grains and silicon oxides (SiO_2, SiO_x, SiO) reported in Ref. [5] were used in the BEMA analysis. SE studies were refereed by measurements of transmission spectroscopy for the evaluation of the film thickness and accompanied by the measurements of RBS, XRD and Raman spectroscopy presented in Table 1.

3. Results and discussion

Fig. 1a shows the experimental SE spectrum of the imaginary part, $<\varepsilon_2>$; of the pseudodielectric function of a nc-Si:Er,O film whose RBS analysis gave an Er content of 4.7% (sample Er3). Different BEMA models have been tested in the fit analysis of this spectrum. It can be seen in Fig. 1a that a two-layer model (model A; dashed curve) which only considers the amorphous, crystalline silicon and SiO components does not provide a good fit, resulting in high values of the fit goodness parameter, χ^2 = 0.89; and of 95% fit parameters confidence limits. Therefore, we concluded that the discrepancy in the calculated spectrum parameters could be related to the unaccounted response of Er impurity. Indeed, after introducing in the BEMA model a dispersion relation based on Lorentzian oscillators describing the dielectric response of erbium ions, a perfect fit, with lower χ^2 = 0.009 and lower errors on fit parameter (layer thickness and constituent volume fractions), was obtained (model B; solid line), yielding a volume fraction of Er of about 5% (see model B), in excellent agreement with the RBS results. The determined dielectric response of erbium ions in a nc-Si/SiO matrix used for the fitting models is shown in the inset of Fig. 1.

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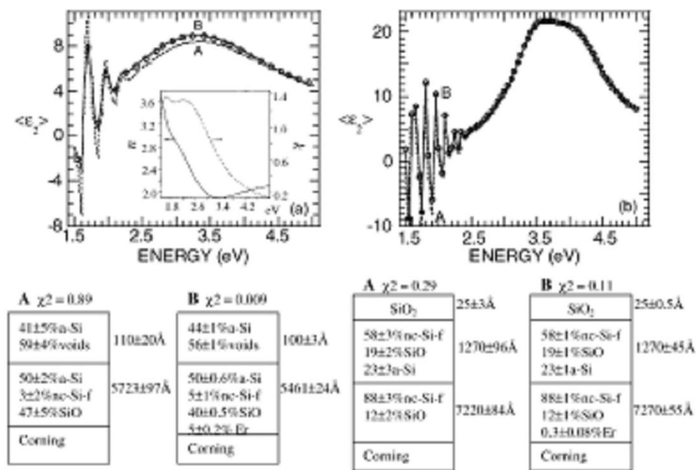

Fig. 1. SE spectra of the imaginary part, $\langle \varepsilon_2 \rangle$, of the pseudodielectric function of samples with (a) high (sample Er3) and (b) low (sample Er12) Er-content. Fit results according to BEMA models with (continuous lines; models B) and without (dashed lines; models A) Erbium inclusion are also shown together with the corresponding BEMA models. The inset shows the optical response (in terms of the refractive index n and extinction coefficient k) of Er ions in the nc-Si/SiO matrix as determined by the least-squares regression analysis using a Lorentzian oscillators based dispersion equation in the high doped sample. The fit goodness, χ^2, and 95% confidence limits of fit parameters are also shown.

The sensitivity of SE to the Er content was also tested in samples with low Er-contents (<1%). Fig. 1b shows the experimental and fit spectra for a sample with 0.2% of Er, as determined by RBS (sample Er12). By the inclusion of a 0.3% volume fraction of Er ions, the fit goodness parameter χ^2 decreases by a factor 3, and also errors on fit parameter decrease (see best fit BEMA models). In this case, the contribution of Er to the fit improvement is better seen in the low energy region (below 2.5 eV) where the optical response of Er reveals the strong absorption (see inset in Fig. 1a). It is worthy to note that the estimations of concentration performed by SE analysis are in good accordance with the RBS values not only for Er but also for O atoms (compare the models and the values in Table 1).

A strong influence of the Er-doping on the nanostructure and optical properties of thin nc-Si films has been found. Fig. 2 contrasts the $\langle \varepsilon_2 \rangle$ spectra of nc-Si films grown in identical conditions with (samples Er12 and Er13) and without (samples Si12 and Si13) Er doping. The #12 and #13 samples only differ in the growth temperature of 350°C and 250°C, respectively. The comparison of SE spectra obtained for both sets shows that the inclusion of Er increases the amplitude of the pseudodielectric function, smoothes and nears the energetic position of the characteristic E_1 and E_2 peaks, which are indicative of the presence in films of the crystalline fraction [6]. The characteristic E1 and E2 peaks (at about 3.4 and 4.2 eV, respectively) become more pronounced in the spectra of undoped samples. Qualitatively, this spectral behavior provides indication on a larger grain size for undoped films, while smaller silicon

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grains are present in Er-doped films. In fact, the BEMA models of the undoped Si12 and Si13 samples include, in the inner and outer layers, the dielectric function of nc-Si-large grains, while the response of Er doped samples is mainly represented by the dielectric function of nc-Si-fine grains (the best-fit BEMA models obtained for these samples are presented at the bottom of Fig. 2.).

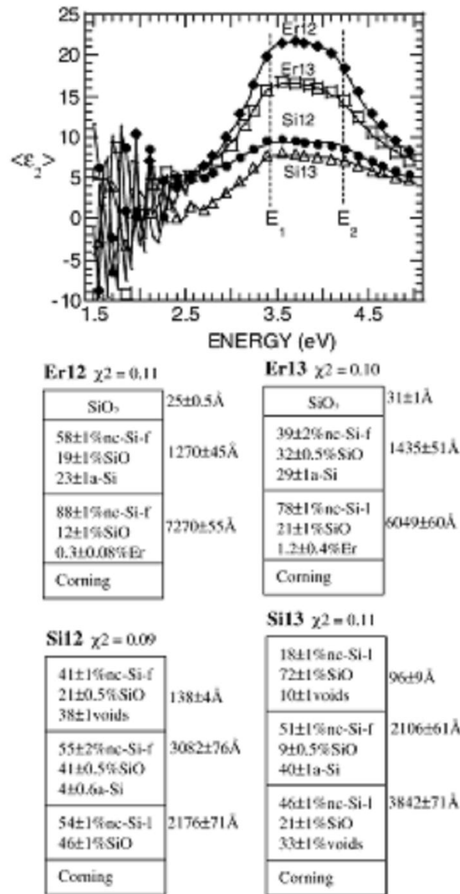

Fig. 2. SE spectra of the imaginary part, $\langle \varepsilon_2 \rangle$, of the pseudodielectric function of samples with (Er12, Er13) and without (Si12, Si13) erbium inclusion. The best-fit results according to BEMA models are presented at the bottom. The fit goodness, χ^2, and 95% confidence limits of fit parameters are also shown.

This effect of the Er-content on the grain size has been confirmed by the X-ray diffraction measurements reported in Table 1, which reveal a strong (about 2 times) decrease of the grain size in samples doped with Er, so corroborating the SE results. In contrast, no variation of the grain size was detected by Raman. However, this apparent discrepancy is explained by the fact that the Raman method only probes the thin near surface layer (within the second outer layer in the BEMA models) in

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the film, where the low-size crystal grain fraction dominates. Therefore, SE is sensitive to structural aspects, such as the different crystalline fraction and grain size in the different layers constituting the nc-Si:Er:O films, which otherwise cannot be resolved by XRD and Raman. In addition, SE data show that the larger grain size accompanies with a larger inclusion of the SiO component, since oxygen segregates at the grain boundaries (see Er12/Si12 samples in Fig. 2). It is thought that this Er effect on the grain size could be related to the preferential incorporation of Er ions into interstitial sites of the silicon network, so causing distortion of the lattice periodicity and obstructing the crystal grain expansion during growth. However, further work is in progress to understand the mechanism of the evolution of nc-Si film structure with Er-doping.

4. Summary

Spectroscopic ellipsometry has been applied to the analysis of the nanostructure and chemical composition of Er-doped nc-Si thin films, produced by the RF magnetron sputtering. In contrast to the standard techniques of X-ray diffraction, Rutherford backscattering and Raman spectroscopy, which provide averaged structural and compositional data, ellipsometry reveals the complex layered structure and impurity distribution in nc-Si:Er,O films. It has been found that the inclusion of Er in nc-Si thin films lowers the Si crystallite sizes in nc-Si thin films. Additionally, SE shows a surprisingly high sensitivity to the Er content as low as 0.2 at%. The optical response of Er ions in a nc-Si/SiO matrix has also been determined.

References

[1] M.F. Cerqueira, M.V. Stepikhova, J.A. Ferreira, Mater. Sci. Eng. B 81 (2001) 32.
[2] E.A. Irene, Thin Solid Films 233 (1993) 96.
[3] D.A.G. Bruggeman, Ann. Phys. (Leipzig) 24 (1965) 636.
[4] G.E. Jellison, Thin Solid Films 313–314 (1998) 33.
[5] M. Losurdo, R. Rizzoli, C. Summonte, G. Cicala, et al., J. Appl. Phys. 88 (2000) 2408.
[6] D.E. Aspnes, A.A. Studna, Phys. Rev. B 27 (1983) 985.

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