Thermal evolution of Er silicate thin films grown by rf magnetron sputtering

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Abstract

Stoichiometric Er silicate thin films, monosilicate (Er_2SiO_5) and disilicate ($Er_2Si_2O_7$), have been grown on c-Si substrates by rf magnetron sputtering. The influence of annealing temperature in the range 1000–1200 °C in oxidizing ambient (O_2) on the structural and optical properties has been studied. In spite of the known reactivity of rare earth silicates towards silicon, Rutherford backscattering spectrometry shows that undesired chemical reactions between the film and the substrate can be strongly limited by using rapid thermal treatments. Monosilicate and disilicate films crystallize at 1100 and 1200 °C, respectively, as shown by x-ray diffraction analysis; the crystalline structures have been identified in both cases. Moreover, photoluminescence (PL) measurements have demonstrated that the highest PL intensity is obtained for $Er_2Si_2O_7$ film annealed at 1200 °C. In fact, this treatment allows us to reduce the defect density in the film, in particular by saturating oxygen vacancies, as also confirmed by the increase of the lifetime of the PL signal.

1. Introduction

Er-doped materials have attracted great attention in Si-based microphotonics, since Er ions emit photons at about 1.54 μm when they are embedded in solid hosts; this is a very interesting wavelength because it corresponds to a minimum in the loss spectrum of silica optical fibers. Er doping is however limited by clustering or segregation; these phenomena are detrimental for the emission properties since Er clusters are optically inactive. The maximum excitable Er concentration strongly depends on the host: for example, it is about 10^{18} cm^{-3} in crystalline Si [1] or 10^{20} cm^{-3} in SiO_2 [2]. This low Er concentration is one of the main limits to obtain optical gain in Er-doped materials. To overcome this limit, a different approach may be represented by Er compounds, such as the oxide Er_2O_3 [3, 4] or the silicates Er_2SiO_5 and $Er_2Si_2O_7$ [5–8], in which Er is not a dopant but a bulk constituent. In these compounds Er concentration is very high, of the order of 10^{22} cm^{-3}; for this reason they are promising materials to obtain high gain coefficient, thus opening the possibility to realize active optical devices, such as waveguides or amplifiers [3, 5]. Although good optical properties have been demonstrated in these Er silicates [5–8], it is well known that rare earth silicates can interact very strongly with Si by means of chemical reactions [9], and this may limit their possible application in Si microphotonics. The understanding of the mechanisms ruling the interaction between silicate films, the outer ambient and the substrate during high temperature annealing processes is then a fundamental step to obtain chemically stable silicate thin films on Si. In this paper we report the influence of high temperature annealing in oxidizing environment on the structural and optical properties of stoichiometric Er silicate thin films (Er_2SiO_5, $Er_2Si_2O_7$) grown on c-Si substrates by magnetron sputtering.

2. Experimental details

Er silicate thin films were prepared by using a UHV magnetron sputtering system. Base pressure before the deposition was about 10^{-9} mbar. Films were grown in an Ar atmosphere (5×10^{-3} mbar) by co-sputtering 4″ diameter and 0.25″ thick water-cooled SiO_2 and Er_2O_3 targets (99.9% purity or higher) arranged in a confocal sputter-up configuration. Films, about 150 nm thick, were deposited on (100) c-Si substrate heated
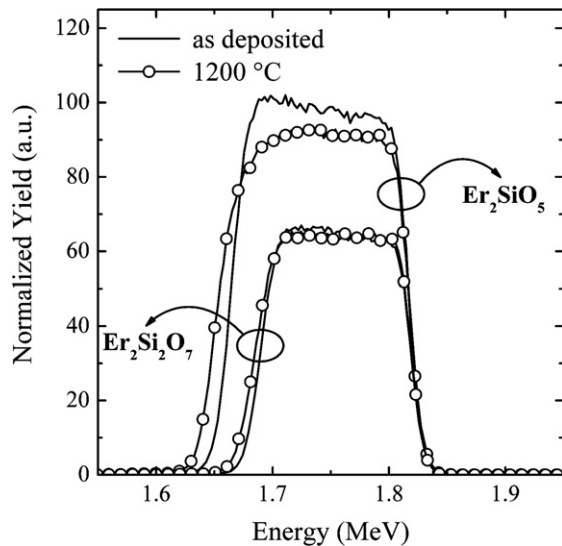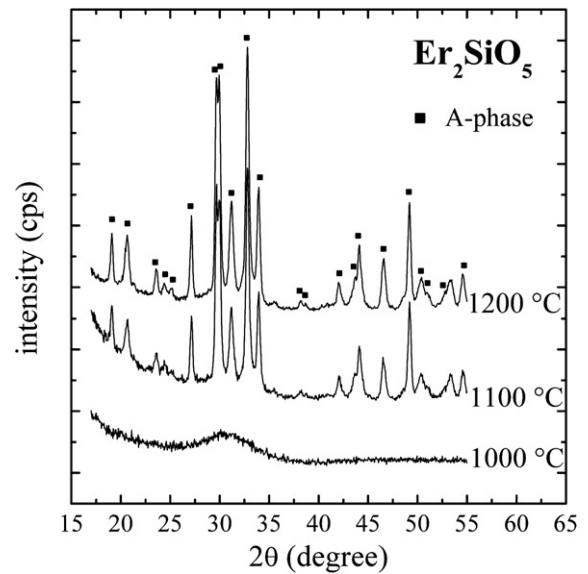
Figure 1. Er RBS signal of Er_2SiO_5 and $Er_2Si_2O_7$ thin films as deposited and annealed at 1200 °C.

Figure 2. XRD spectra of Er_2SiO_5 films after thermal treatments at 1000, 1100 and 1200 °C; the spectra have been offset for clarity. The solid squares associated with the peaks refer to the A phase of Er_2SiO_5 (JCPDS file no 70-3279).

at 400 °C. The two stoichiometric Er silicates Er_2SiO_5 and $Er_2Si_2O_7$ were synthesized by appropriately varying the radio-frequency (rf) power applied to the SiO_2 target, 150 and 350 W, and by keeping a constant rf power of 200 W to the Er_2O_3 target. After the deposition, the samples were thermally treated for 30 s in O_2 ambient in the temperature range 1000–1200 °C in a rapid thermal annealing (RTA) system. Rutherford backscattering spectrometry (RBS) measurements were carried out in a HVEE singletron accelerator by using a 2.0 MeV He$^+$ beam in random configuration with the detection placed at an angle of 165° with respect to the incident beam in order to measure the film composition. Glancing angle x-ray diffraction (XRD) analysis was performed with a Bruker AXS D5005 diffractometer using Cu Kα radiation with a grazing incidence angle of 1.0°. Photoluminescence (PL) measurements were performed by pumping with the 476.5 and 488 nm lines of an Ar$^+$ laser having a pump power of 10 mW, and the laser beam was chopped through an acousto-optic modulator at a frequency of 11 Hz. The PL signal was analyzed by a single grating monochromator and detected by a liquid-N$_2$-cooled Ge detector. Spectra were recorded with a lock-in amplifier using the acousto-optic modulator frequency as a reference. All the spectra have been corrected for the spectral system response. Time resolved PL measurements were performed by first detecting the modulated luminescence signal with a Hamamatsu infrared-extended photomultiplier tube and then analyzing the signal with a photon counting multichannel scaler. The overall time resolution of the system is 30 ns.

3. Results and discussion

RBS analyses have been performed on the as deposited samples to investigate their chemical composition. The elemental concentration of Er, Si and O is uniform along the whole film thickness for both samples. The atomic ratio is Er:Si:O = 2:1:5 for the film obtained by using 150 W rf power to the SiO_2 target (we will refer to this sample as

Er_2SiO_5), and Er:Si:O = 2:2:7 for that obtained using 350 W rf power to the SiO_2 target (we will refer to this sample as $Er_2Si_2O_7$). Since chemical reactions that can occur during the annealing between film, substrate and ambient are typically thermally activated and thus temperature dependent, we have studied the compositional evolution of the two silicate films after annealing processes. Figure 1 shows Er RBS signals of the two silicates before (solid line) and after (solid line and open circles) a thermal process at 1200 °C.

In the case of the monosilicate Er_2SiO_5, the Er profile appears almost unchanged after the annealing even if a slight broadening and a lower Er content on the low energy side (i.e. near the interface with silicon) are observed. Therefore, most of the layer keeps its starting composition while a thin interfacial layer having an $Er_2Si_2O_7$ composition forms. Its formation can be explained by supposing that Er_2SiO_5 reacts with Si diffusing from the substrate to the film and with O diffusing into the film from the outer atmosphere through the thermodynamically favored reaction $Er_2SiO_5 + SiO_2 \rightarrow Er_2Si_2O_7$. Its occurrence is further confirmed by the formation of a thin SiO_2 layer between the film and the substrate. Instead, for the disilicate $Er_2Si_2O_7$ the Er signal is fully unchanged and the initial stoichiometry is preserved owing to the fact that Si diffusion is inhibited by the absence of interfacial chemical reactions, since no Er silicate having higher SiO_2 content exists and only the formation of a thin SiO_2 layer at the interface with the substrate has been observed. Therefore, reactions between Er silicate films and Si substrate, also for high temperature treatments in reactive ambient, are strongly limited in the case of an initial stoichiometric composition (mono- or disilicate), and in particular they are totally absent for $Er_2Si_2O_7$.

Structural properties have been studied by XRD analysis. Both as deposited films are amorphous, while crystallization occurs after the thermal treatments. XRD spectra of annealed Er_2SiO_5 are shown in figure 2.
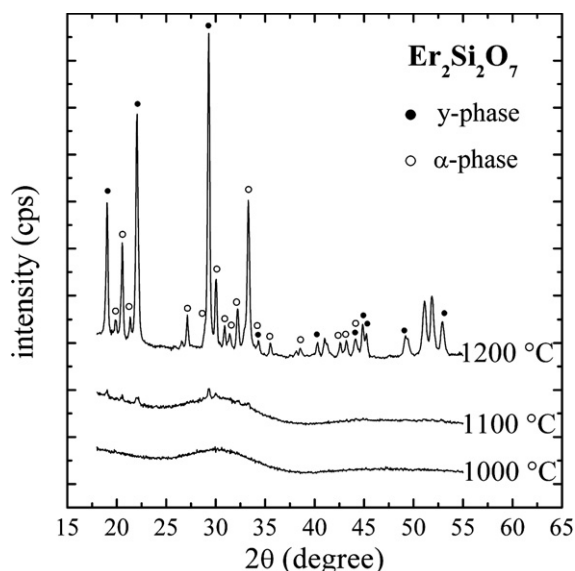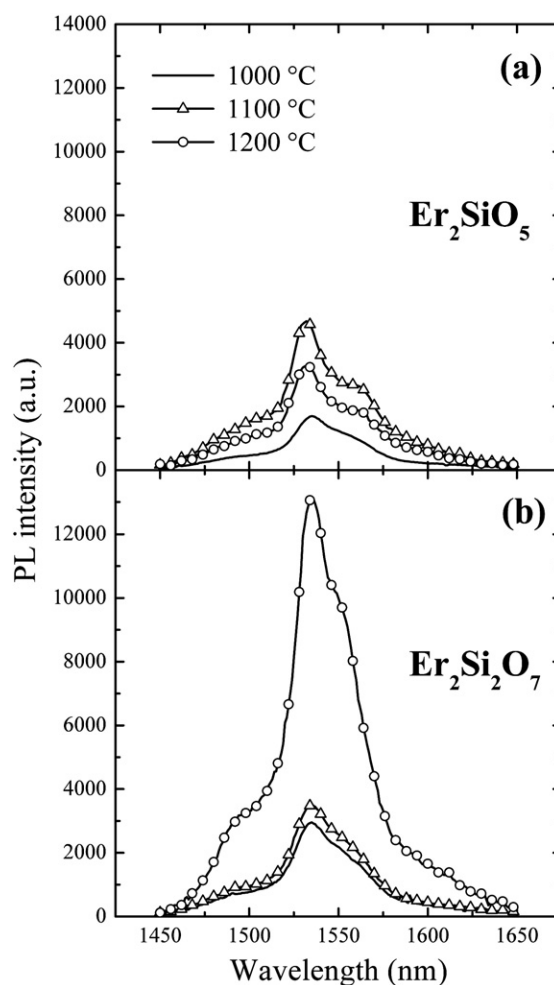
Figure 3. XRD spectra of $Er_2Si_2O_7$ films after thermal treatments at 1000, 1100 and 1200 °C; the spectra have been offset for clarity. Symbols associated with the peaks refer to the y phase of $Y_2Si_2O_7$ (solid circles) (JCPDS file no 74-1994) and to the α phase of $Tm_2Si_2O_7$ (open circles) (JCPDS file no 31-1391).

Er_2SiO_5 films are still amorphous after the annealing at 1000 °C, as indicated by the presence of only a broad peak around 30°; after the 1100 °C annealing this structure is not visible anymore, but many diffraction peaks appear, demonstrating the occurrence of crystallization. The same diffraction peaks with the same intensities are found in the sample treated at 1200 °C: crystallization is therefore already complete at 1100 °C. It is well known that rare earth monosilicates exhibit two different polymorphs depending on the synthesis temperature, named A and B phases, with the former obtained at lower temperature. All the diffraction peaks in figure 2 correspond to those of the A phase of Er_2SiO_5 (JCPDS file no 70-3279), having a monoclinic structure (space group $P2_1/c$) [10]; peaks belonging to the B phase are absent. Moreover, the formation of the A phase from Er/Si/O mixtures treated at the same temperature has been previously reported [5, 11, 12]. Finally, although RBS analysis shows evidence of the formation of an interfacial $Er_2Si_2O_7$ layer, no diffraction peaks corresponding to this compound are observed, thus suggesting that this layer is amorphous.

The thermal evolution of O_2-annealed $Er_2Si_2O_7$ thin films is very different, as shown in figure 3.

Also in this case the film remains amorphous after the treatment at 1000 °C; in samples annealed at 1100 °C some very weak diffraction peaks appear, thus indicating that a partial crystallization is occurring. After the annealing at 1200 °C the same peaks become much more intense and other less intense peaks appear. Concerning the formed crystalline structure, it is well known that all rare earth disilicates show up to four different polymorphs depending on the formation temperature, named y, α, β and γ; moreover, it has been observed that for other rare earth disilicates the crystallization as y or α phase or as a mixture of them may occur in the temperature range 900–1200 °C [13–16]. Unfortunately,

Figure 4. Room temperature PL spectra obtained for (a) Er_2SiO_5 and (b) $Er_2Si_2O_7$ films after thermal treatments at 1000, 1100 and 1200 °C. The excitation wavelength is 488 nm and the pump power is 10 mW.

no powder diffraction files of y or α phases of $Er_2Si_2O_7$ exist in the JCPDS reference database, but by comparing the XRD spectrum of figure 3 with indexed diffraction patterns concerning other rare earth disilicates it is possible to associate the observed peaks with those of the y phase of $Y_2Si_2O_7$ (JCPDS file no 74-1994) (monoclinic cell, space group $P2_1/m$) and of the α phase of $Tm_2Si_2O_7$ (JCPDS file no 31-1391) (triclinic cell, space group P-1). This is possible since structural data of rare earth disilicates strictly depend on the ionic radius of the rare earth ion; in the case of Er^{3+}, Tm^{3+} and Y^{3+} they are very similar, being 0.88 Å, 0.89 Å and 0.90 Å, respectively [14]. It is then possible to conclude that $Er_2Si_2O_7$ crystallizes at 1200 °C as a mixture of y and α phases.

We have studied the room temperature light emission in the infrared region from the silicate films by exciting them with the 488 nm line of an Ar^+ laser having a power of 10 mW. This wavelength is resonant with the $^4I_{15/2} \rightarrow \, ^4F_{7/2}$ transition of Er ions. As deposited samples show a very weak PL signal peaked at about 1.54 μm, due to the $^4I_{13/2} \rightarrow \, ^4I_{15/2}$ radiative transition. Higher PL intensities are observed for all the annealed samples; the spectra are shown in figures 4(a) and (b) for Er_2SiO_5 and $Er_2Si_2O_7$, respectively.

Er$_2$SiO$_5$ exhibits a PL intensity increase by a factor of about 2.5 on increasing the annealing temperature from 1000 to 1100 °C, that can be associated with the film crystallization. Instead a slight PL intensity decrease for 1200 °C annealing temperature is observed, probably due to the above discussed formation of an amorphous interfacial Er$_2$Si$_2$O$_7$ layer at the expense of Er$_2$SiO$_5$, not contributing to the photon emission. Instead, Er$_2$Si$_2$O$_7$ shows almost the same PL intensity on passing from 1000 to 1100 °C, followed by a steep increase by a factor of four on increasing the annealing temperature to 1200 °C. Also in this case the highest PL emission is obtained for the annealing temperature that induces the film crystallization. Finally we observe that, for the best annealing conditions, Er$_2$Si$_2$O$_7$ shows an integrated PL intensity higher by a factor of three than that observed in Er$_2$SiO$_5$; this effect is associable with the longer lifetime of 152 μs (recorded at 1.54 μm) exhibited by Er$_2$Si$_2$O$_7$ with respect to the value of 32 μs measured for Er$_2$SiO$_5$. The shorter lifetime of Er$_2$SiO$_5$ is probably due to the presence of defects which cannot be recovered even by employing the optimal annealing conditions and limit the PL efficiency of this material. For this reason we have examined in more detail the optical properties of Er$_2$Si$_2$O$_7$.

We have hence performed PL analysis by using a pump power of 10 mW with an excitation wavelength of 476.5 nm, which is not resonant with any atomic transitions of Er ions. While only a weak signal is observed for samples annealed at 1100 and 1200 °C under these excitation conditions, a more intense PL emission is recorded for samples annealed at 1000 °C. The ratio between PL intensities obtained under both non-resonant and resonant excitation conditions is reported in figure 5(a) as a function of the annealing temperature.

This ratio is very small, about 0.03, for the samples annealed at 1100 and 1200 °C, thus meaning that Er ions are mainly excited resonantly, as expected. Instead this ratio is about 0.25 in the case of the lowest studied annealing temperature, demonstrating that in this case Er ions can be excited also non-resonantly; for both excitation conditions PL spectra have identical shapes, as shown in figure 5(b), thus suggesting that in both cases the emitting Er ions have the same environment. This unexpected energy transfer mechanism is attributable to the presence of oxygen vacancies that can act as sensitizers for Er, thus absorbing and transferring the energy to nearby Er ions, as recently demonstrated in Er-doped HfO$_2$ films [17]. In order to confirm that this sensitization is occurring also in our disilicate films, the PL emission of a Er$_2$Si$_2$O$_7$ sample annealed for 30 s at 1200 °C in N$_2$ ambient has been studied: in this case oxygen vacancies in the film cannot be saturated during the thermal treatment and, indeed, the PL emission observed under non-resonant excitation is more intense, the ratio between PL intensities under the two excitation conditions being equal to 0.5. These results demonstrate that in reactive ambient an annealing temperature of 1100 °C is necessary to ensure an efficient oxygen diffusion during the thermal treatment and the complete saturation of oxygen vacancies inside the Er$_2$Si$_2$O$_7$ film.

The influence of defects on the optical properties of silicate films is further confirmed by the analysis of the
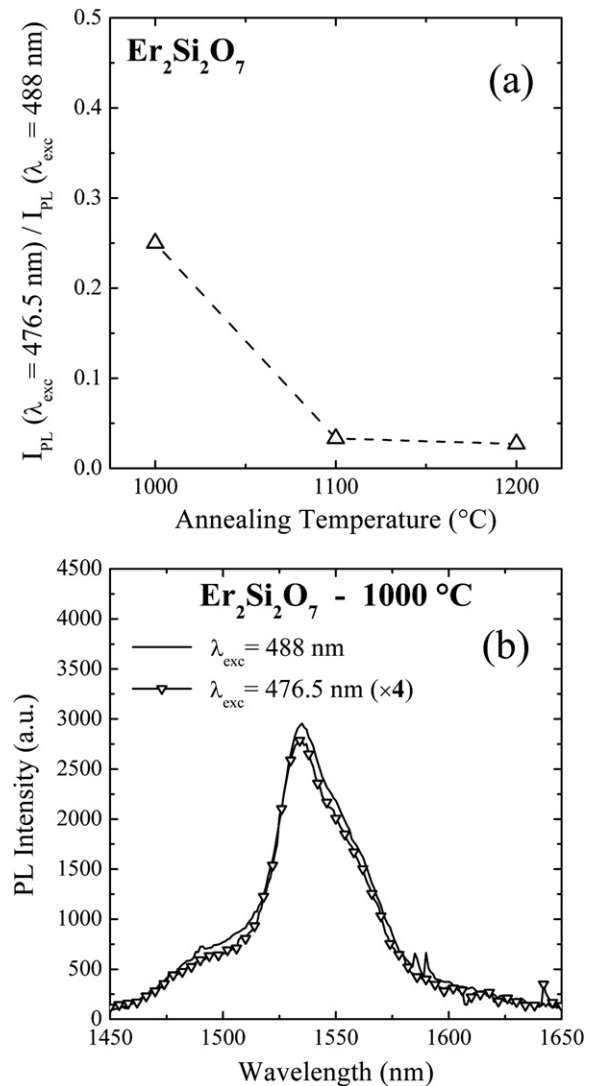
Figure 5. (a) Ratio between PL intensity obtained exciting non-resonantly (476.5 nm) and resonantly (488 nm) Er$_2$Si$_2$O$_7$ films. (b) PL spectra for Er$_2$Si$_2$O$_7$ annealed at 1000 °C obtained under both resonant and non-resonant excitation conditions.

decay time of PL signals at 1.54 μm. In fact, in erbium silicate the high Er content necessarily involves a very small mean Er–Er distance, by leading to strong Er–Er interactions and to the migration of the excitation inside the material (known as concentration quenching), hence the non-radiative Er de-excitation mechanisms through defects are very probable and typically observed lifetime values are lower than those in common Er-doped systems (of the order of milliseconds) [2, 5–8]. We have recorded lifetime values of 38 μs and 61 μs for Er$_2$Si$_2$O$_7$ samples annealed at 1000 and 1100 °C, respectively. The longer lifetime observed for samples treated at 1100 °C confirms the efficient saturation of oxygen vacancies at this temperature. By increasing further the annealing temperature from 1100 to 1200 °C the lifetime increases from 61 to 152 μs, probably due to the crystallization-induced reduction of the density of other kinds of defect, and the PL emission is maximized. Then it is possible to conclude that both oxygen diffusion in the layer and

crystallization are fundamental requirements in order to reduce defect density inside $Er_2Si_2O_7$ films and, in turn, to optimize the optical properties.

4. Conclusions

The study of the structural and optical properties of the two stoichiometric erbium silicates (Er_2SiO_5 and $Er_2Si_2O_7$) as a function of annealing temperature in the range 1000–1200 °C has been performed. RBS analysis has shown that both films are chemically stable also after reactive annealing (O_2) at 1200 °C; in particular, only in the case of Er_2SiO_5 a thin interfacial $Er_2Si_2O_7$ layer is formed. By XRD measurements it has been demonstrated that Er_2SiO_5 and $Er_2Si_2O_7$ crystallize at 1100 °C and 1200 °C, respectively; in particular, Er_2SiO_5 crystallizes in the A phase of Er_2SiO_5 while $Er_2Si_2O_7$ forms a mixture of y and α phases of $Er_2Si_2O_7$. Intense photon emissions at 1.54 μm from the annealed crystalline samples have been observed. The highest PL efficiency has been obtained for $Er_2Si_2O_7$ films annealed at 1200 °C, since this process is able to efficiently suppress the oxygen vacancies, responsible for undesirable defect-mediated luminescence, and other non-radiative defects.

Acknowledgments

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