Photoluminescence performance of pulsed-laser deposited $\text{Al}_2\text{O}_3$ thin films with large erbium concentrations

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Erbium doped $\text{Al}_2\text{O}_3$ films with concentrations up to $6 \times 10^{20}$ Er cm$^{-3}$ have been prepared in a single step process by pulsed-laser deposition. Alternate ablation of $\text{Al}_2\text{O}_3$ and Er targets has been used to control the in-depth distribution and in-plane concentration of Er$^{3+}$ ions independently. The characteristic Er$^{3+}$ photoluminescence response at 1.53 $\mu$m has been studied as a function of the Er$^{3+}$ distribution. It is found that lifetime values can be greatly increased by increasing the Er$^{3+}$–Er$^{3+}$ in-depth separation above 3 nm. This result can be related to a reduced Er$^{3+}$–Er$^{3+}$ energy migration process. The in-plane Er$^{3+}$ concentration was increased by either increasing the number of pulses on the Er target or the laser energy density for ablation. By the latter method in-plane concentrations as high as $1.1 \times 10^{14}$ Er cm$^{-2}$ per layer (corresponding to $2 \times 10^{20}$ Er cm$^{-3}$) were achieved, while keeping lifetime values as high as 6 ms. This result is explained in terms of shallow Er$^{3+}$ implantation during deposition. © 2001 American Institute of Physics. [DOI: 10.1063/1.1409575]

I. INTRODUCTION

After the success of the Er-doped silica fiber amplifier at 1.5 $\mu$m, the Er-doped planar optical waveguide amplifier has received great attention as it will be one of the key elements for the development of high performance integrated optical circuits on silicon. The fabrication of small integrated devices opens new challenges to the material design, since in the planar optical amplifiers only a few centimeters are available, compared with the tenths of meters available in the fiber optical amplifier. Due to the relatively small emission cross section of the first Er$^{3+}$ excited state it has been calculated that to achieve amplification the concentration of optical active Er$^{3+}$ ions has to be in the $10^{20}$ ions cm$^{-3}$ range. Both effects depend partially on the nature of the host material and, moreover, they depend strongly on the so-called microscopic distribution of the Er$^{3+}$ ions in the host material. Recently, comparing the performance of two integrated planar amplifiers, one prepared by ion implantation and the other by co-sputtering, it has been suggested that in order to achieve efficient amplification it is essential to optimize the preparation method to obtain an homogeneous Er$^{3+}$ ion distribution. In this work, pulsed-laser deposition (PLD) is used for the synthesis of Er-doped thin films. This technique has proven to be excellent for the preparation of complex oxide structures. PLD involves high kinetic energy species which enable the production of high density films with good adhesion. These unique features make PLD a very attractive technique for the deposition of high quality films for optical applications. Lately PLD is being successfully used for the preparation of Er-doped thin films of a wide range of materials including semiconductors, and glasses. In these works a single Er-doped target is used as source material and there are no precise means to control the desired Er$^{3+}$ concentration and distribution. A similar situation is found for the many works in which sputtering from a single target has been used. In our previous works we have followed a different approach to prepare Er-doped thin films based on the use of two separate targets of pure Er and $\text{Al}_2\text{O}_3$ that are alternately ablated. In this way the concentration of each film can be designed in each deposition experiment. Moreover, we have shown that the Er$^{3+}$–Er$^{3+}$ in-depth separation can be controlled and that it has an important influence on the photoluminescence (PL) response of the films. It should be mentioned that chemical methods, such as plasma enhanced chemical vapor deposition and sol-gel, have also been used for the preparation of $\text{Al}_2\text{O}_3$ thin films with Er$^{3+}$, but they do not allow tailoring of the Er$^{3+}$ ion distribution.

The aim of this work is to demonstrate that alternate PLD allows us to obtain thin $\text{Al}_2\text{O}_3$ films with large Er concentration and enhanced photoluminescence performance. Aluminum oxide ($\text{Al}_2\text{O}_3$) has been chosen as a host material because waveguide fabrication technology has been deve-
oped, and high-quality low loss waveguides are readily made on silicon using lithographic techniques. The high contrast in reactive index of Al₂O₃ and the SiO₂ cladding layer leads to a high confinement of the guided light, making possible small device structures. The Al₂O₃ Er-doped films are prepared in a single-step process, with independent control of the number of laser pulses and laser energy density for each of the Al₂O₃ and Er targets allowing tailoring of both the in-depth and in-plane Er³⁺ ion distribution. Furthermore, it will be shown that a controlled nonhomogeneous distribution of the Er³⁺ ion distribution can yield good luminescence performance of the films.

II. EXPERIMENT

The thin films were deposited in vacuum (10⁻⁷ Torr) on chemically cleaned Si (100) wafers held at room temperature. An ArF excimer laser (λ=193 nm, τ=20 ns full width at half maximum) was used to ablate the Al₂O₃ and Er targets. These were mounted in a computer-controlled holder which permits their alternate ablation. The Al₂O₃ deposition cycle was repeated a number of times (up to 400), the final deposition always being Al₂O₃ in order to protect the active ions from reactions with air. The total Er content as well as its concentration depth profile were varied from sample to sample by varying the ratio of the number of laser pulses on the Al₂O₃ target to that on the Er one, and the laser energy density on the Er target. The latter was modified by selectively inserting an attenuator at the laser output only when the Er target was to be ablated. The film thickness was controlled during growth by in situ reflectivity measurements. After deposition, the films were annealed in air in 50 °C steps from 600 to 850 °C to improve their photoluminescence response. Annealing of the films above 850 °C led to surface damage and deterioration of the photoluminescence performance.

The Er concentration and in-depth profile distribution were measured by Rutherford backscattering spectrometry (RBS) using a 2.0 MeV He⁺ beam and a scattering angle of 165°. It was checked that the abovementioned annealing procedure does not cause any significant change in the measured Er profile distribution of the films.

PL measurements were made at room temperature using a single grating monochromator (focal length 250 mm) with a wavelength resolution of 2.5 nm, a liquid-nitrogen cooled Ge detector, and standard lock-in techniques. The 514.5 nm line of an Ar⁺ ion laser (power 140 mW) chopped at 10 Hz was used as the excitation source, the incident beam forming an angle of 25° with the sample normal. The emitted light was collected along the direction perpendicular to the film. Luminescence decay curves at the peak of the emission spectrum were averaged and recorded with a digital oscilloscope.

III. RESULTS

The RBS spectra of the PLD erbium-doped films have the same general features as the RBS spectrum shown in Ref. 13. The part of the spectrum corresponding to the Er profiles indicates that approximately flat concentrations throughout the Al₂O₃ film have been obtained within the resolution of the measurement. In pulsed-laser deposited Al₂O₃ doped with metal nanocrystals we have previously observed a well-defined layered structure at the sub-nm scale, showing no significant diffusion of the dopant into the matrix under our deposition conditions. We expect therefore that the incorporated Er³⁺ ions are distributed in layers, one per growing cycle, not resolvable by RBS. It is worth noting that there are no traces of impurities. Other preparation methods may introduce impurities into the films: for example, the Ar, used as sputter gas in the case of radio-frequency magnetron sputtering and the impurities from precursors in the case of the sol-gel preparation.

In order to obtain quantitative information from the RBS spectra, the total Er areal density was determined with 5% accuracy using a Bi-implanted amorphized Si standard. Subsequently the spectra were simulated using the RUMP code to obtain the atomic areal density of the amorphous Al₂O₃. From these data the film thickness was determined using the density of our amorphous aluminum oxide, which has been experimentally determined to be (8.7±0.8)×10⁻²³ cm⁻³, and thus slightly less dense than crystalline Al₂O₃. The total thickness for all the films studied in this work is maintained constant at a value of 270±20 nm.

The PL performance of three different series of samples has been studied in this work. In each of these three series, the Er content of the films has been varied from sample to sample by modifying one deposition parameter while keeping constant values for the others. In the first series, the number of Er layers included in the films varies from 33 to 400, with the number of pulses and energy density per pulse on the Er target fixed respectively at 1 pulse and 2 J cm⁻², this resulting in the distance between two consecutive layers varying from 0.6 to 9.0 nm. In the second and third series the Er layer separation is maintained constant at ~2.6 and 5.4 nm, respectively, but the Er concentration per layer is varied in two different ways. For the second series the number of pulses on the Er target in each cycle is varied from 1 to 4 with a constant energy density of 2 J cm⁻² per pulse, while for the third series the laser energy density on the Er target is varied from 2 to 5 J cm⁻² with the number of pulses fixed at a 1 per layer.

Figure 1 summarizes the values obtained for the total Er areal density and its distribution (Er³⁺–Er³⁺ layer separation and Er per layer areal density) for each series as a function of the number of Er layers included in the film, the number of pulses on the Er target, and the laser energy density on the Er target, respectively. The plotted values have been obtained as follows. The total Er areal density is the value directly determined from the RBS analysis, the Er³⁺–Er³⁺ layer separation is calculated by dividing the total film thickness by the number of cycles used to deposit the film, and the Er areal density per layer is the measured total Er areal density divided by the number of cycles used to deposit the film. As can be seen in Fig. 1(a), the total Er areal density can be increased linearly by increasing each of the three different parameters: the number of Er layers, or the numbers of pulses on Er per layer, or the laser energy density on the Er target. In Fig. 1(b) it is shown that, as expected, the Er layer separation decreases as the number of Er layers increases.
while it does not depend on the number of pulses per layer or on the laser energy density on the Er target. The series grown as a function of the number of pulses per layer has 100 cycles while that as a function of the laser energy density has 50 cycles and thus the latter has an in-depth $\text{Er}^{3+}-\text{Er}^{3+}$ distance twice than the former. Finally the areal density per layer for the different films is seen in Fig. 1. The series of films prepared as a function of the number of Er layers shows a fairly constant Er areal density per layer, whereas in the two other series the Er areal density per layer increases linearly with the number of pulses on the target or with the laser energy density on the Er target, respectively. Thus we have devised two different ways of modifying the Er in-plane concentration.

All the as-grown films exhibit a weak PL emission whose spectrum shows the characteristic peak at around 1.53 $\mu$m corresponding to the transition between the $^4I_{13/2}$ and $^4I_{15/2}$ states of Er$^{3+}$ ions. The thermal annealing procedure causes an increase of both the PL intensity and lifetime which has been explained in terms of defect removal. Thus in the following we will refer to the results obtained for the annealed films.

Figure 2 shows the dependence of both the PL intensity at 1.53 $\mu$m and the lifetime, as a function of the Er$^{3+}-\text{Er}^{3+}$ layer in-depth separation in the range 0.6–9.0 nm. These results were partially published in a previous article and now they have been extended for smaller Er layer separation values. As the Er$^{3+}-\text{Er}^{3+}$ in-depth separation increases, the PL intensity decreases. This is consistent with the fact that the larger the in-depth separation layer the lesser the total number of Er$^{3+}$ ions. The PL lifetime increases and it is confirmed that a saturation is reached for a separation value of about 6 nm. The largest lifetime value is 7.1 ms.

For the other two studied series of films, the in-depth Er distribution remains constant, while its plane concentration is modified. The evolution of the PL intensity and lifetime for these series are plotted against the Er areal density per layer in Fig. 3. The PL intensity increases as the Er areal density per layer increases, and therefore as the total number of Er$^{3+}$ ions in the film increases [see Fig. 1(a)]. The PL lifetime behavior with respect to the Er areal density per layer is different depending on how this increase is obtained. It shows a decreasing trend when the number of pulses on the Er target increases. On the contrary, there is a clear increase of the lifetime when the laser energy density on the Er
target is increased, reaching a saturation value above $8 \times 10^{13}$ Er cm$^{-2}$ per layer.

Figure 4 presents the dependence of the PL intensity on the pump power, measured for the series of films made with different numbers of Er layers. The dashed lines show the linear extrapolation of the first two data points. At higher pump intensities the measured PL intensity curves start to deviate from the linear extrapolation. At 1.2 W corresponding to an intensity of $\sim 150$ kW/cm$^2$ on the sample the signal from the sample with Er$^{3+}$–Er$^{3+}$ separation of 0.6 nm is 10% lower than the linear extrapolation. The deviation is the same for all the studied films. The PL lifetimes do not depend on the power up to 1.2 W. The same behavior as a function of the pump power, namely a deviation from the linear extrapolation for the PL intensity and no change for the lifetime, has been found for the other series of studied films.

In order to analyze the PL performance of all the PLD films regardless of their deposition conditions, the obtained PL values have been plotted as a function of the Er average volume concentration, i.e., assuming the equivalent Er concentration as it would be if the Er$^{3+}$ ions were homogeneously distributed throughout the film. Figure 5(a) shows the PL intensity measured for each film and divided by the total Er areal density ($I_{PL}/[\text{Er}]$), i.e., the PL intensity per incorporated Er$^{3+}$ ion, and Fig. 5(b) shows the PL lifetime. It can be seen that, in this study, high Er concentrations, up to $6 \times 10^{20}$ Er cm$^{-2}$, have been achieved. As shown in Fig. 5(a), the PL intensity per incorporated ion for concentration values higher than $3 \times 10^{20}$ cm$^{-3}$ is similar for all the available films, either prepared with a different number of layers or with a different number of pulses per layer. For low concentrations, the intensity values depend on the preparation conditions. The PL intensity per incorporated Er$^{3+}$ ion seems to be higher for the series of films prepared as a function of the number of layers. The longest lifetime values are found for the films of the first series prepared with a low number of Er layers and for the films of the third series prepared with a high laser energy density on the Er target. It can be deduced from the figure that films with good PL performance (high PL intensity and lifetime) can be found for Er concentrations around $2 \times 10^{20}$ Er cm$^{-3}$.

IV. DISCUSSION

The above results clearly show that the PL response of the PLD films strongly depends on the precise Er distribu-
tion, which can be varied by changing the preparation conditions. For the first series of samples the Er concentration per layer has been maintained almost constant at 3.5–4.5 \times 10^{13} \text{Er cm}^{-2} [see Fig. 1(c)] and only the number of Er layers has been varied. This is quite a high local concentration since it means that the average in-plane Er^{3+}–Er^{3+} ion separation is 1.6 nm. Hence no improvement in the lifetime should be expected for the films with Er^{3+}–Er^{3+} in-depth separations larger than 2 nm, since in a first approximation the luminescence quenching should be dominated by the Er^{3+}–Er^{3+} in-plane interaction. Nevertheless, Fig. 2(b) shows that, although the close in-plane packing of the Er^{3+} ions is maintained for the films in which the Er^{3+}–Er^{3+} in-depth separation is above 3 nm, there is an important increase of the lifetime value for Er^{3+}–Er^{3+} in-depth separations up to 6 nm, where a saturation is found. This result suggests that, in spite of the high local in-plane concentration, the PL quenching can be controlled by choosing an adequate Er^{3+}–Er^{3+} separation in the perpendicular direction. The price that is paid is a moderate decrease in the total Er volume concentration.

In the second series of samples, films grown as a function of the number of pulses on the Er target, the PL intensity increases as a consequence of the increase of the Er areal density per layer, and thus the total number of incorporated Er^{3+} ions. The PL lifetime is found to decrease, suggesting that in this case the PL response is dominated by in-plane concentration quenching. Note that for the film grown with four pulses the average in-plane distance is about 0.8 nm.

Concentration quenching of the Er^{3+} PL may occur by up-conversion processes or by excitation energy migration. Up-conversion can be disregarded in our case as being responsible for the Er concentration dependence of the lifetime because the PL emission intensity has been found to grow linearly with the excitation pump power at least up to a power value of 200 mW and the PL lifetime does not change. The most likely Er^{3+}–Er^{3+} interaction contributing to the lifetime decrease is thus excitation migration, by which some of the excited Er^{3+} ions transfer their energy to a nearby unexcited Er^{3+} ion, luminescence extinction occurring when some of the latter ions are coupled to defects acting as quenching sites. A typical defect found in Er-doped films is the hydroxyl ion (OH− complex), whose stretch vibration is resonant with the Er^{3+} transition from the first excited state to the ground state, and has been shown to be responsible for luminescence quenching in thin films grown by metalorganic chemical vapor deposition and sol gel.

Preliminary Fourier transform infrared absorption measurements in our films show no traces of OH− complexes, thus suggesting that they are at low concentration.

For the films prepared varying the laser energy density on the Er target and a single pulse (third series), the PL lifetimes are longer than in the films prepared using several pulses at a fixed energy density [second series, Fig. 3(b)]. This can be partially explained by the fact that the separation between Er layers (5.4 nm) is larger than in the previous case [2.6 nm, Fig. 1(b)]. However, the trend of the lifetime evolution with the Er areal density in the third series films is opposite to that of the second series films: an increase of the lifetime is observed as a function of the areal density and a saturation is reached for Er areal densities per layer of about 8 \times 10^{13} \text{cm}^{-2}. For areal densities as large as 11 \times 10^{13} \text{cm}^{-2} the measured lifetimes do not decrease. Note that this areal density is equivalent to an Er^{3+}–Er^{3+} in-plane average distance of 1.0 nm, very similar conditions to those found for the second series of films. This lifetime behavior is opposed to the expected concentration quenching when the Er areal density increases, therefore a new process is clearly occurring. It is well known that PLD involves high kinetic energy species (E > 150 eV). In our system for laser energy densities of a few mJ cm^{-2} it has been found that the velocities of the ablated species are typically around 1.4 \times 10^4 \text{m s}^{-1}. Taking into account the mass of Er the estimated kinetic energy of the species arriving at the substrate can be as large as 175 eV. TRIM simulations show that 175 eV Er^{3+} ions reach a depth of 1 nm from the Al2O3 surface. So a possible explanation for the behavior observed in the samples prepared with the largest laser energy densities per pulse (>3 J cm^{−2}) could be the fact that a low-depth Er implantation is achieved during the PLD processes, and thus the Er^{3+} ions cannot be considered deposited on the surface of the Al2O3 layers. It can be suggested that this shallow implantation prevents the formation of very high in-plane Er density areas, and thus the energy migration processes occurring between coupled Er^{3+} ions are reduced. The lower the laser energy density the lower the kinetic energy of the Er^{3+} ions arriving at the Al2O3 surface. For the lowest laser energy densities (<1 J cm^{−2}) no Er implantation at all takes place, thus a flux of Er^{3+} ions arrives and remains at the surface; in these conditions the formation of Er^{3+} clusters may take place. For most of the films studied in this article (first and second series) the laser energy on the target (∼2 J cm^{−2}) is such that a very limited implantation can occur (depth ≤0.5 nm) and effectively the initial assumption that the Er^{3+} ions are deposited on the Al2O3 layer still holds.

V. CONCLUSIONS

It has been demonstrated that PLD is an excellent technique to prepare Er-doped thin films with high dopant concentrations. Good control of the dopant distribution (concentration and profile) can be achieved in a single production step. Lifetimes longer than 6 ms for an average Er concentration in the order of 10^{20} \text{cm}^{-3} can be obtained when the Er–Er in-depth separation is larger than 3 nm and the Er in-plane concentration is about 10^{14} \text{cm}^{−2} per layer, the Er being deposited with a high laser energy density (>3 J cm^{−3}) on the Er target. When high laser energy density is used for PLD, probably the local distribution of Er^{3+} ions is altered, avoiding the formation of clusters at the Al2O3 surface. The fact that by adequately choosing the PLD deposition parameters the Er distribution can be adjusted has interesting implications in building of gain waveguide devices. For example, films with an Er distribution to fit the propagation mode could be prepared, and as we have seen they can have high Er local concentrations where needed without a deterioration of the overall luminescence performance.
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