In situ growth of optically active erbium doped Al_2O_3 thin films by pulsed laser deposition

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Thin Al_2O_3 films are grown and *in situ* doped with erbium by pulsed laser deposition in a single step process, by alternate ablation from Al_2O_3 and Er targets. The as-deposited films have an Er step dopant profile throughout the film thickness, whose concentration depends on the number of pulses at the Er target. The as-grown films are optically active, as evidenced by the photoluminescence spectrum centered at 1.533 μm, corresponding to intra-4f transitions in Er^{3+}. The photoluminescence intensity increases upon annealing due to an increase of the luminescence lifetime. This is most likely a result of a decrease in the nonradiative decay channels, related to annealing of defects in the Al_2O_3 film. © *1996 American Institute of Physics.* [S0003-6951(96)02837-9]

Good quality active optical materials have to be developed in thin film form in order to achieve integrated optoelectronic devices for the photonic technology. Since the success of the optical fiber amplifier, rare-earth doped optical materials for waveguides are being studied because of their potential application as planar optical amplifiers and lasers.[1] The rare earth ion Er^{3+} is particularly suitable for these applications due to its intra-4f transitions around 1.5 μm, a standard communications wavelength. The feasibility of obtaining active thin films by Er incorporation has led to an intensive research on materials such as glasses,[2,3] Al_2O_3,[4] $LiNbO_3$,[5] or silicon.[6] Al_2O_3 is an interesting material for waveguides because its relative high index respect to SiO_2 cladding layers allows to confine light very well in the waveguide, making small devices feasible.[7] Furthermore, Al_2O_3 is especially suitable for Er doping since the similarity in valency and lattice constants between Al_2O_3 and Er_2O_3 allows for incorporation of high concentrations of Er in the Al_2O_3 structure. Very recently, a low-loss compact Er doped Al_2O_3 waveguide amplifier has been produced, using sputtering deposition followed by multiple ion implantation.[8]

Ion implantation has been successfully used for rare earth incorporation in materials for waveguides,[2,4,8,9] nevertheless it is a technique that involves at least a two-step process for the production of doped thin films: deposition and implantation. Furthermore, implantation leads to a high density of defects in the material, and therefore postannealing is imperative. In addition, during annealing at high temperatures the short range diffusion of the Er may allow the formation of new structural phases or precipitates.[9] To overcome these difficulties, a single-step process involving both deposition and dopant incorporation is desirable. Pulsed laser deposition (PLD) is a recently developed technique which has been very successfully applied for the deposition of complex oxide films with complicated structures.[10] Conceptually and from the point of view of the experimental requirements, it is a very simple and low cost technique. It is, in principle, a stoichiometric technique and produces high density films with good adhesion thanks to the presence of energetic species during the deposition process. These unique features make PLD a very attractive technique for the deposition of high quality thin films for optical applications.[11] It has been successfully applied to produce a variety of glass thin films, such as chalcogenide films exhibiting interesting photoinduced effects,[12] or CdTe microcrystallite doped glasses with nonlinear optical properties.[13] More recently, it has been used to successfully produce Er doped phosphate glasses,[14] or $LiNbO_3$.[15] Al_2O_3, due to its high optical transparency, and excellent properties as an electrical insulator, is a material with significant technological importance, and therefore it is not surprising to find very early reports on Al_2O_3 growth by PLD using either ruby or transversely excited atmosphere (TEA) CO_2 lasers.[16–18] Only in one case,[17] were the optical properties studied, and the films showed a relatively poor oxidation state, high absorption, and a relatively low refraction index. In this letter we describe not only the successful deposition of Al_2O_3 films with good optical properties by PLD but also the incorporation of optically active Er during growth by alternate ablation of Er and Al_2O_3 targets in a single-step process.

Pulsed laser deposition was performed in a vacuum chamber with a base pressure of 4×10^{-7} mbar. The beam of an ArF excimer laser [Questek 2440, 193 nm, 20 full width at half maximum (FWHM)] was focused onto the targets, leading to energy densities of about 3 J/cm^2 per pulse. The Al_2O_3 (99.9%) and Er (99%) targets were mounted on a computer controlled multiple holder which allowed to expose alternatively each of them to the laser beam. Both targets were rotated during deposition in order to avoid crater formation and droplet particles emission during ablation. The deposition sequence was 40 pulses on the Al_2O_3 target and two on the Er target, and it was repeated 400 times. The substrates were chemically cleaned Si(100) wafers and they were held at room temperature during deposition. The target-substrate distance was 32 mm. A low power HeNe laser (632.8 nm) focused onto the substrate was used to perform *in situ* reflectivity measurements during growth, which allowed us to control the growth process, and determine the sample thickness, deposition rate, and the film refractive index ($\mathbf{n}=n+ik$) at 632.8 nm.[14] The films were grown up to a thickness

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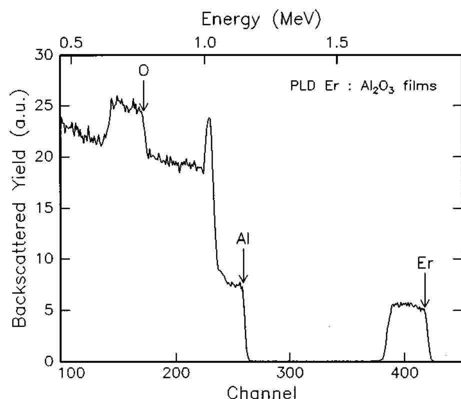

FIG. 1. RBS spectrum of an Al_2O_3 film doped with Er during pulsed laser deposition. The surface channels of the different elements are indicated.

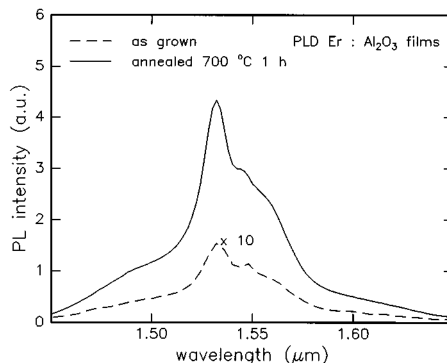

FIG. 2. Room-temperature PL spectrum (spectral resolution 6.5 nm) of an Al_2O_3 film doped with Er during pulsed laser deposition, both for the as-grown film and after annealing at 700 °C during 1 h.

of 200 nm at the substrate center. The average deposition rate was 0.06 nm/s for a laser frequency of 5 Hz. The changes in the film reflectivity measured during deposition fit well with an n value of 1.68 and very low absorption ($k<0.005$). This n value is among the highest reported in the literature for deposited Al_2O_3 films,[7] and it is not far from that of simple crystal Al_2O_3 ($n=1.76$ ordinary ray).[19] This result indicates that the film density is quite high, as expected for PLD films,[11] and films grown in our experimental conditions seem to be denser than those produced by PLD using a TEA CO_2 laser.[17]

The Er concentration profiles were measured by Rutherford backscattering spectrometry (RBS) using a 2.0 MeV He^+ beam and a scattering angle of 150°. Figure 1 shows the RBS spectrum of an Al_2O_3 film doped with Er grown by alternate laser ablation. The arrows indicate the surface channels of the different elements. The peak at channel 229.5 is due to the overlapping of the Al signal from the Al_2O_3 layer with the Si signal from the underlying substrate. Using this peak, and assuming the density of bulk Al_2O_3, the thickness of the film was determined to be 190 mm, which is in very good agreement with that obtained from the *in situ* reflectivity measurements. The Er profile, from 384 to 418 channels, is flat, and shows that Er is distributed throughout the film thickness. The areal density of Er is 1.9×10^{16} atoms/cm^2, which corresponds to an average concentration of 1 at. %. From these data, 5.7×10^{15} and 4.8×10^{13} atoms/cm^2 are deposited in each step from the Al_2O_3 and Er targets, respectively. These figures suggest that about 1/2 of a monolayer of alumina is roughly grown in each step, and only 1% of this amount of Er is then deposited on top. Therefore, Er clustering is very unlikely under these deposition conditions, and a good dopant homogeneity is expected. Finally, note that there are no traces of other elements in our pulsed laser deposited films, whereas incorporation of Ar, used as sputter gas, was detected in the films grown by radio frequency magnetron sputtering.[4]

Photoluminescence (PL) measurements were performed at room temperature using a 48 cm single grating monochromator and a liquid nitrogen-cooled Ge detector. The 514.5 nm line of an Ar^+ ion laser was used as excitation source. The pump power was 60 mW over a 1.5-mm-diam spot. The PL intensity was measured by chopping the excitation beam (12 Hz) and monitoring the detector signal using a lock-in amplifier. A thermal anneal at 700 °C in vacuum (base pressure $<10^{-6}$ mbar) during 1 h was performed for half of each studied sample. The PL spectra of both the as deposited and the annealed films can be seen in Fig. 2. In both cases, the spectrum shows a peak at 1.533 μm corresponding to intra-4f transitions between the $^4I_{13/2}$ (first excited) state and the $^4I_{15/2}$ (ground) state of Er^{3+}. The peak structure of the spectrum is attributed to Stark splitting of the degenerate 4f levels, characteristic of Er^{3+} incorporated in a solid. This spectrum is similar to that reported elsewhere for Al_2O_3 films doped with Er by ion implantation.[4] The PL spectrum of the as-grown sample exactly overlaps the one of the annealed sample when multiplied by a factor of 28. This indicates that no significant changes in the chemical surrounding of the luminescent Er ions take place upon annealing, as these changes should affect the Stark splitting and therefore the spectrum peak structure.

In order to determine the origin of the PL intensity enhancement, luminescence decay measurements were performed. The pump beam was chopped at 12 Hz, resulting in a block-shaped pump pulse of 10 ms. The PL signal at the peak of the spectrum (1.533 μm) was monitored and averaged using a digital oscilloscope as the beam was switched off. Figure 3 shows the PL decay results on both the as-grown and annealed samples. As can be seen, a single exponential decay is observed in both cases, with a 1/e decay time

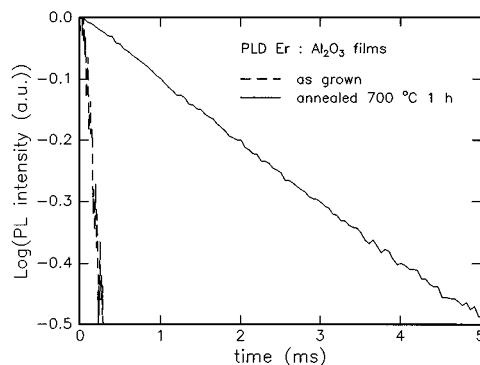

FIG. 3. PL decay curves after an excitation pulse, for an Al_2O_3 film doped with Er during pulsed layer deposition, both for the as-grown film and after annealing at 700 °C during 1 h.

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of 0.2 μs and 4.4 ms for the as-grown and the annealed samples, respectively. The PL intensity and lifetime are related through rate equations governing the excitation and decay of the excitable Er ions. Assuming that excitation into the $^2H_{1/2}$ manifold (514.5 nm) is followed by rapid decay to the first excited state, the PL intensity of the $^4I_{13/2} -> ^4I_{15/2}$ transition at a fixed pump intensity and wavelength is proportional to the density of active Er ions, the pump absorption cross section, and to the ratio τ/τ_r, where τ and τ_r are the measured and the radiative lifetimes, respectively. These lifetimes are related through the equation

$$1/\tau = 1/\tau_r + 1/\tau_{nr}, \quad (1)$$

where τ_{nr} is the nonradiative lifetime. Thus, the existence of nonradiative decay channels will lead to a measured lifetime τ smaller than the radiative lifetime, τ_r.

Since the increase in the PL intensity (Fig. 2) upon annealing is approximately the same as the increase in the measured lifetime (τ) [Fig. 3], it can be deduced that the density of active Er ions remains approximately constant, and also does τ_r.[4,9] Hence, Eq. (1) suggests that changes in lifetime are mainly due to changes in the nonradiative lifetime τ_{nr}. The observation that the shape of the PL spectrum does not change upon annealing further supports this reasoning. The increase of τ therefore can be explained by a decrease in the number of nonradiative decay channels, such as those provided by defects in the film. The measured lifetime in the pulsed laser deposited films is high compared to that reported for Er implanted Al_2O_3 sputter deposited films at similar concentrations (fluence 10^{16} Er/cm^2, Er peak concentration 1.0 at. %) and annealed at slightly higher temperatures (825 °C).[4] This comparison is very positive taking into account that in our case the 1 at. % Er concentration is distributed throughout the whole thickness of the film and not only at the peak, as it is in the case of the implanted films.

The results presented in this letter show that pulsed laser deposition is a promising technique to produce Er active waveguides. When compared to the procedure of sputtering film deposition and doping by multiple Er ion implantation, which has been used to fabricate a successful Er doped waveguide amplifier,[8] several advantages can be mentioned. First, alternate PLD simultaneously allows film growth and doping, in a single-step process and therefore reduced costs are expected. Second, alternate PLD Er doped Er films have the potential to easily design dopant distributions adapted to the optical mode propagating in the waveguide, a result that in the case of ion implanted films requires multiple ion implantation ranging from 100 KeV to 1.5 MeV.[8] Finally, although the as-deposited films show nonradiative decay channels for the Er PL, it is to be expected that further research in the deposition conditions (i.e., oxygen environment, substrate temperature, and target/substrate distance) may lead to the *in situ* growth of defect free Al_2O_3 films with optimized luminescence.

In conclusion, optically active Er-doped Al_2O_3 thin films have been prepared by alternate pulsed laser ablation from Al_2O_3 and Er targets in a single-step process. It has been shown that this technique allows to design a uniform and efficient dopant distribution throughout the film thickness. The as-deposited films show clear Er-related PL at 1.5 μm, and a further increase of the PL intensity and the lifetime (4.4 ms) can be achieved by postdeposition annealing, which is related to a decrease in the number of nonradiative decay channels.

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