Broadband sensitization of 1.53 μm Er^{3+} luminescence in erbium-implanted alumina

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Experimental evidence of an efficient broadband sensitization mechanism in erbium-implanted alumina is presented. Alumina thin films were deposited by plasma-enhanced chemical vapor deposition using trimethyl-amine alane and nitrous oxide. The as-grown films, together with sapphire crystals, were implanted with erbium. Photoluminescence excitation spectra showed that erbium-implanted sapphire crystals exhibit characteristic Er^{3+} luminescence at 1.53 μm only when pumped resonantly. In contrast, erbium-implanted alumina thin films exhibit 1.53 μm luminescence even when pumped at wavelengths outside Er^{3+} absorption bands. We postulate that the sensitizing species is either small nanoclusters of aluminum or pairs of aluminum ions. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1829139]

Rare-earth doped materials are of key importance in optical communication systems, as demonstrated by the dominance of the erbium-doped fiber amplifier. Rare-earth doping of planar optical waveguides offers the promise of active devices, such as optical amplifiers, with shorter waveguides than fiber-based systems.[1–4] Currently, there is much interest in integrated optical components based on planar waveguides for the implementation of wavelength division multiplexing (WDM) in fiber-to-the-home systems.[5] Opportunities for such components include WDM sources, optical multiplexing and de-multiplexing, wavelength conversion, flatband filters, optical amplifier gain equalization, routers, optical cross-connects, and receivers.

Recently, Er^{3+}-doped waveguide amplifiers have found applications in metropolitan WDM optical networks. This is mainly due to their smaller size and reduced cost compared to erbium-doped fiber amplifiers (EDFAs). EDFA optical topologies include high-power laser diodes at either 980 or 1480 nm; these laser diodes constitute a large proportion of the EDFA cost, and thus the development of a broadband pumped Er^{3+} system would yield significant savings. Currently, pump lasers for EDFAs retail in the \$500–\$1000 range,[6] whilst high power broadband sources such as light emitting diodes (LEDs) can cost as little as \$10–\$20, with prices falling rapidly.

Several groups have reported a coupling mechanism between luminescent rare-earth ions and semiconductor nanocrystals.[7–9] Moreover, studies have shown that this coupling considerably enhances the effective absorption cross section of the rare-earth ions. This enhancement can be up to four orders of magnitude in the case of Er^{3+} in silicon-rich silica.[10] Potentially, this mechanism may relax requirements on the pump wavelength for Er^{3+}-doped optical amplifiers, leading to the realization of broad-band pumpable optical amplifiers at the important telecommunications wavelengths around 1.55 μm; recent reports have suggested gain of up to 3 dB cm^{-1} from such material pumped using a blue LED.[11] In addition, it has also been reported that it is possible to sensitize erbium emission in silica in a similar fashion using co-implantation with silver.[12] For a recent review of different mechanisms for sensitization of erbium luminescence in planar amplifiers, see Ref. 13.

Alumina has also attracted attention as a host for rare-earth ions due to the high solubility and broad emission linewidth (55 nm) that Er^{3+} exhibits when incorporated in Al$_2$O$_3$.[3,4,14,15] Erbium-doped alumina thin films have been fabricated using various techniques, including plasma-enhanced chemical vapor deposition (PECVD),[14] reactive co-sputtering,[4] and ion implantation.[16] A net optical gain of 2.3 dB has been reported from a 4-cm-long Er^{3+}-implanted Al$_2$O$_3$ optical waveguide pumped with 9 mW of power at 1.48 μm.[3]

In this study, we report experimental evidence of an indirect excitation mechanism for rare-earth ions in Er^{3+}-implanted alumina.

Alumina thin films 700 nm thick were deposited on Si (100) substrates by PECVD. A detailed description of the apparatus used for the deposition of the thin films can be found elsewhere.[17] The films were deposited using trimethyl-amine alane (TMAA) as the aluminum precursor, and nitrous oxide as the oxidizing agent. Argon was used as the carrier gas for the Al precursor. The stoichiometry of the thin films was controlled by varying the Ar/TMAA to N$_2$O flow rate ratio. The as-deposited thin films, together with single sapphire crystals, were then implanted with erbium. In order to achieve a uniform erbium depth distribution in the alumina layer, two implantation energies were employed: 50 and
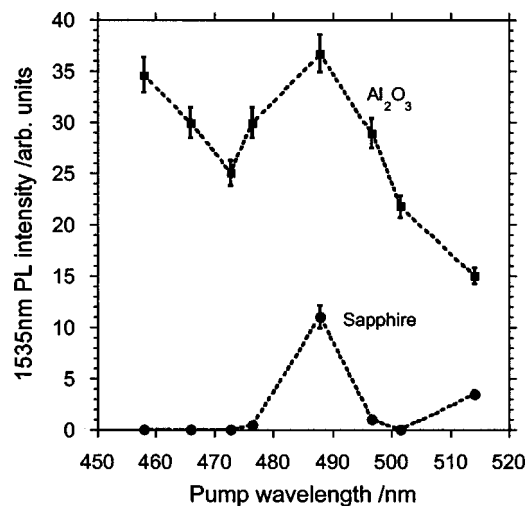

FIG. 1. Photoluminescence excitation spectra of erbium-implanted sapphire and erbium-implanted PECVD-grown alumina. Laser power at the sample ≈ 50 mW, spot size=1 mm, monochromator resolution=1 nm. Dotted lines are guides for the eye.

FIG. 2. Electron energy loss spectrum of an erbium-implanted PECVD-grown alumina film.

150 keV (implantation fluences ranged from 6.0×10^{14} to 2.5×10^{15} Er/cm^2). The peak erbium concentration was measured by Rutherford backscattering spectrometry, and was found to be 0.5 at. % (1.3×10^{20} cm^{-3}). The implanted samples were thermally annealed at 850 and 950 °C for 90 min in nitrogen in order to optically activate the Er^{3+} and enhance the photoluminescence intensity at 1.53 μm by removing implantation-induced defects. The samples were analyzed structurally using Auger emission spectroscopy (AES), Fourier transformed infrared spectroscopy (FTIR), transmission electron microscopy, and electron energy-loss spectroscopy. Photoluminescence (PL) and PL excitation (PLE) spectra were measured at room temperature using eight visible lines from an Ar$^+$ laser, a single grating monochromator, and standard lock-in techniques. An InGaAs photodiode and a photomultiplier tube were used to detect near-infrared and visible spectra, respectively.

The AES depth profile of as-grown, undoped alumina thin films deposited by PECVD showed them to be slightly aluminum rich (~ 4 at. % excess aluminum) with very low carbon contamination. A detailed account of the structure and the surface quality of the undoped PECVD-deposited thin films can be found elsewhere.[17]

Figure 1 shows photoluminescence excitation spectra of an erbium-implanted sapphire crystal and an erbium-implanted PECVD-deposited alumina thin film, both thermally annealed at 900 °C for 90 min following implantation. Care was taken to maintain constant laser power for each pump wavelength. All samples were implanted with the same erbium concentration (0.5 at. %) under identical conditions. It is evident that the erbium-implanted sapphire crystal exhibits PL only when pumped at wavelengths that correspond to Er^{3+} absorption bands (488 and 514.5 nm). Emission is, in this case, due to direct optical excitation of the Er^{3+} ions from the ground state ($^4I_{15/2}$) to the $^4F_{7/2}$ and $^2H_{11/2}$ levels via the absorption of pump photons at 488 and 514.5 nm, respectively. In contrast, erbium-implanted PECVD-grown alumina thin films exhibit PL even when pumped at wavelengths far away from Er^{3+} absorption bands, although there is still a strong element of direct absorption (note the PL peak at 488 nm). This behavior indicates coupling between
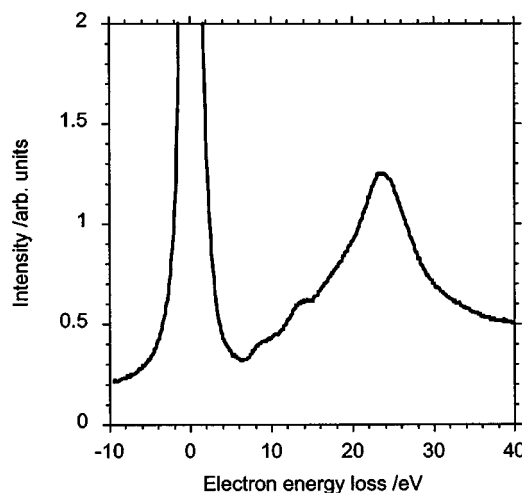
the alumina host and the Er^{3+} ions. This effect is similar to the coupling that exists between Er^{3+} and Si nanocrystals in silicon-rich silica thin films.[7–9]

Figure 2 shows an electron energy loss spectrum (EELS) of an erbium-implanted alumina sample. The main plasmon peak at around 23 eV corresponds to Al$_2$O$_3$, and an additional shoulder is present at an energy loss of 14–15 eV. The full width at half maximum of the zero-loss peak was 1 eV in the EELS measurements. The shoulder is present in spot-EELS spectra recorded from throughout the alumina layer, and from some locations a separate peak is resolved at this energy. There is no clear correlation between the strength of the peak and structural features in the film. The aluminum and erbium plasmon excitations are both expected to be close to 14–15 eV, so these EELS spectra may indicate the presence of a low concentration of metallic clusters.

It is known that implantation of alumina with metallic ions can in some cases lead to the formation of aluminum precipitates via a reduction mechanism.[18] In a study by Hunt *et al.*, it was determined that aluminum clusters can be precipitated if the free energy of the following reaction, where X is a rare-earth ion, is negative:

$$2X + Al_2O_3 \rightarrow 2Al + X_2O_3.$$
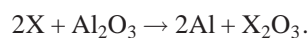
Using values for enthalpies of formation and entropies given in standard reference texts,[19] we calculate from Eq. (1) that the Gibbs free energy for the reduction of alumina by erbium is negative (-218.6 kJ mol^{-1}), so it is feasible that some aluminum clusters are formed.

$$\Delta G = \Delta H - T\Delta S. \tag{1}$$

However, in the present case no definitive evidence of the existence of nanoclusters in the alumina matrix could be found, though the AES depth profile and FTIR indicate that the film is slightly aluminum-rich. It should be noted that in the study reported in Ref. 18, the peak concentration of implanted rare-earth ions was very high—approximately 9 at. %. This is much greater than the concentration used in our study, and may explain the difficulty in discerning a clear peak in the EELS spectra attributable to aluminum clusters.

Figure 3 shows visible PL spectra for films as-grown and following thermal annealing at 850 and 950 °C after implantation with erbium. From this figure, it is evident that the defect-related peak at 2.2 eV has been considerably in-
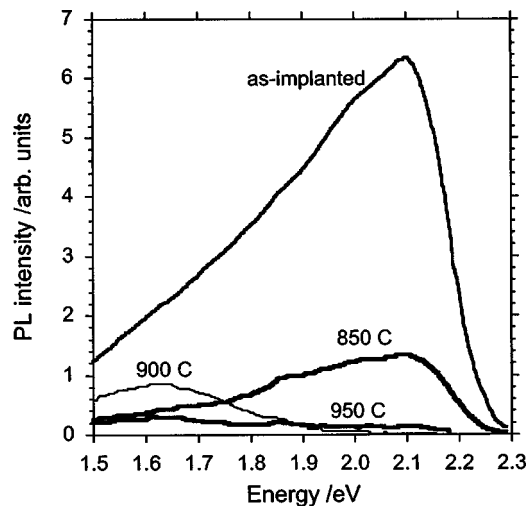
FIG. 3. Photoluminescence spectra of a PECVD-grown alumina film as-grown and following annealing at 850, 900, and 950 °C. Laser power at the sample ≈50 mW, spot size=1 mm, monochromator resolution=2 nm.

creased by annealing at 850 °C. This can be explained by an increase of the number of dangling bonds in the alumina matrix after the reduction of –OH that takes place at 650 °C. After annealing at 900 and 950 °C, the peak at 2.2 eV is

quenched due to structural rearrangement compensating the dangling bonds in a similar way to that seen in silicon-rich silica.[20] This suggests that the sensitization is not due to implantation-related defects in the alumina matrix—a conclusion supported by the lack of sensitization in implanted single crystal sapphire.

Figure 4 shows the PL intensity from the Er^{3+}-implanted PECVD-deposited alumina thin films as a function of pump power. Two pump wavelengths are chosen: 488 nm corresponding to direct optical excitation, and 476 nm, which is predominantly indirect excitation. When pumped nonresonantly, the Er^{3+} PL saturates at approximately 4.0×10^{19} photons/cm² s. In contrast, resonant pumping does not produce saturation even at a flux of 6.0×10^{20} photons/cm² s. This implies either a small concentration of the sensitizing species, or a large effective absorption cross section for indirect excitation.

In summary, a broadband sensitization mechanism for erbium luminescence in polycrystalline alumina films has been demonstrated. Although there is no conclusive evidence of aluminum clusters in this material, we speculate that the sensitization may be either due to such nanoclusters present at a very low concentration, or else to a species generically similar to that seen in silver-activated erbium-doped borosilicate glass, in which absorption is thought to be due to pairs of silver atoms.[12] Further work is needed to conclusively identify the sensitizing species; nevertheless, this mechanism is another promising route to broadband excitation of erbium-doped optoelectronic devices.
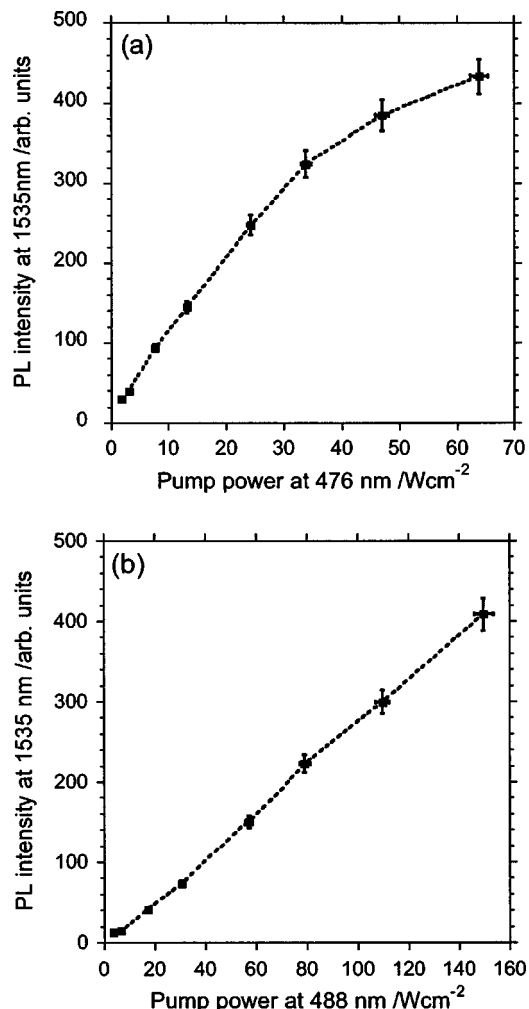
FIG. 4. Photoluminescence at 1535 nm as a function of pump laser power for an erbium-implanted PECVD-grown alumina film. (a) Pump wavelength=476 nm (indirect excitation), (b) pump wavelength=488 nm (resonant excitation). Laser spot size=1 mm. Dotted lines are guides for the eye.

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