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# Enhancement of photoluminescence from Yb and Er co-doped $\text{Al}_2\text{O}_3$ films by an asymmetric metal cavity

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The effects of Au thin layers on luminescence properties of Er and Yb co-doped  $\text{Al}_2\text{O}_3$  films were studied. The  $1.54\ \mu\text{m}$  emission of  $\text{Er}^{3+}$  excited by the energy transfer from  $\text{Yb}^{3+}$  is found to be strongly enhanced by placing a Au layer on top of the films. Photoluminescence excitation spectra of the  $1.54\ \mu\text{m}$  PL of  $\text{Er}^{3+}$  and time transients of the 980 nm emission of  $\text{Yb}^{3+}$  revealed that PL enhancement arises from two different mechanisms. The first one is the enhancement of local electric fields accompanied by the excitation of surface plasmons of rough Au surfaces. The other one is the enhancement of energy transfer rate from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  caused by the modification of the local photonic mode density at the position of the Yb–Er coupled system. © 2006 American Institute of Physics. [DOI: 10.1063/1.2166685]

The emission property of an emitter can be significantly modified if it is placed in a microcavity or in the vicinity of metal surface.<sup>1–3</sup> The simplest explanation of the phenomenon is that the emitter is regarded as an electromagnetic dipole oscillator, interacting with the reflected field of the emitter's dipole radiation.<sup>4</sup> If the reflected field interacts with the emitter in phase, the radiative decay rate is enhanced, while out of phase, it decreases. As a result, the radiative rate oscillates with the distance between the emitter and the surface. The other explanation of the phenomenon is that the local photonic mode density (PMD) is changed in the vicinity of metal surface, and this results in the modification of the radiative rate, because it is proportional to PMD.<sup>4</sup> The modification of PMD is considered to affect the rate of Förster energy transfer as well,<sup>5–7</sup> although the mechanism is not very clear.<sup>8</sup> The control or the enhancement of Förster energy transfer is of great importance for a lot of fields in which sensitized excitation of optically forbidden transitions of an acceptor by the energy transfer from a donor is required.

One of the examples of the Förster energy transfer is sensitized excitation of Er by the energy transfer from Yb. Er has trivalent ionic states ( $\text{Er}^{3+}$ ) in solid matrices, and shows atomic-like sharp luminescence at around  $1.54\ \mu\text{m}$  due to the intra-4f shell transition.<sup>9–11</sup> Since the wavelength corresponds to the minimum loss band of silica optical fibers, the Er-doped silica fiber amplifier (EDFA) is now a standard device for long-distance optical telecommunication. The intra-4f shell transition is parity forbidden for dipole transition. The radiative rate as well as the absorption cross section are thus very small. To overcome the small absorption cross section and realize sufficient amplification, very long fibers are used in EDFA. Another approach to overcome this problem is to simultaneously dope photosensitizers in glasses and to excite  $\text{Er}^{3+}$  indirectly by the energy transfer from the sensitizers. A typical photosensitizer for  $\text{Er}^{3+}$  is  $\text{Yb}^{3+}$ .<sup>12–16</sup> In the inset of Fig. 1(a), the process of sensitized excitation of  $\text{Er}^{3+}$  by  $\text{Yb}^{3+}$  is shown schematically.  $\text{Yb}^{3+}$  has only one excited

state in the 4f shell at 980 nm, which exactly coincides with the excitation energy of  $\text{Er}^{3+}$  to the second excited state. Since absorption cross section of  $\text{Yb}^{3+}$  is much larger than that of  $\text{Er}^{3+}$ , in the co-doped system, excitation light at 980 nm is absorbed mainly by  $\text{Yb}^{3+}$ , and then the electronic excitation is transferred to the second excited state of  $\text{Er}^{3+}$  by the Förster mechanism.

The purpose of this work is to obtain enhanced  $1.54\ \mu\text{m}$  emission from  $\text{Er}^{3+}$  for Er and Yb co-doped glasses by controlling local electric fields and PMD by placing a thin metal layer on top. The samples studied are  $\text{Al}_2\text{O}_3$  films containing Er and Yb (Er:Yb: $\text{Al}_2\text{O}_3$ ). We will demonstrate that by placing a Au layer, PL intensity is strongly enhanced, and discuss the mechanism from photoluminescence excitation (PLE) spectra of the  $1.54\ \mu\text{m}$  PL of  $\text{Er}^{3+}$  and time transients of the 980 nm PL of  $\text{Yb}^{3+}$ .

Samples were prepared by a co-sputtering method.<sup>17,18</sup>  $\text{Al}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$  were simultaneously sputter-deposited on quartz substrates in Ar gas. The thickness of films was fixed to be about 130 nm for all the samples. To activate Er, deposited films were annealed in air for 30 min at 900 °C. In this work, we fixed Yb concentration to about 0.06 at. % and changed Er concentration from 0 to 0.14 at. %. After the annealing, Au thin films (25 or 67 nm) were deposited on the Er:Yb: $\text{Al}_2\text{O}_3$  films. Atomic force microscope observations revealed that rms roughnesses of 0.7 and 1.1 nm exist on the surfaces of the 25 and 67 nm thick Au films, respectively. To take PL and PLE spectra, and time transients of PL, an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser (pulse width 5 ns, repetition frequency 20 Hz) was used as an excitation source, and a liquid nitrogen cooled Ge photodiode or near infrared photomultiplier (Hamamatsu, R5509-72) for the detection of near-infrared emission from  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ . The excitation wavelength was changed from 450 to 1050 nm.

The PLE spectra detected at  $1.54\ \mu\text{m}$  for the Er:Yb: $\text{Al}_2\text{O}_3$  and Er: $\text{Al}_2\text{O}_3$  samples are shown in Fig. 1(a). Several peaks corresponding to electronic excitation of  $\text{Er}^{3+}$  can be seen. By doping Yb, the PLE peak at 980 nm grows significantly and a broad band appears in the range between

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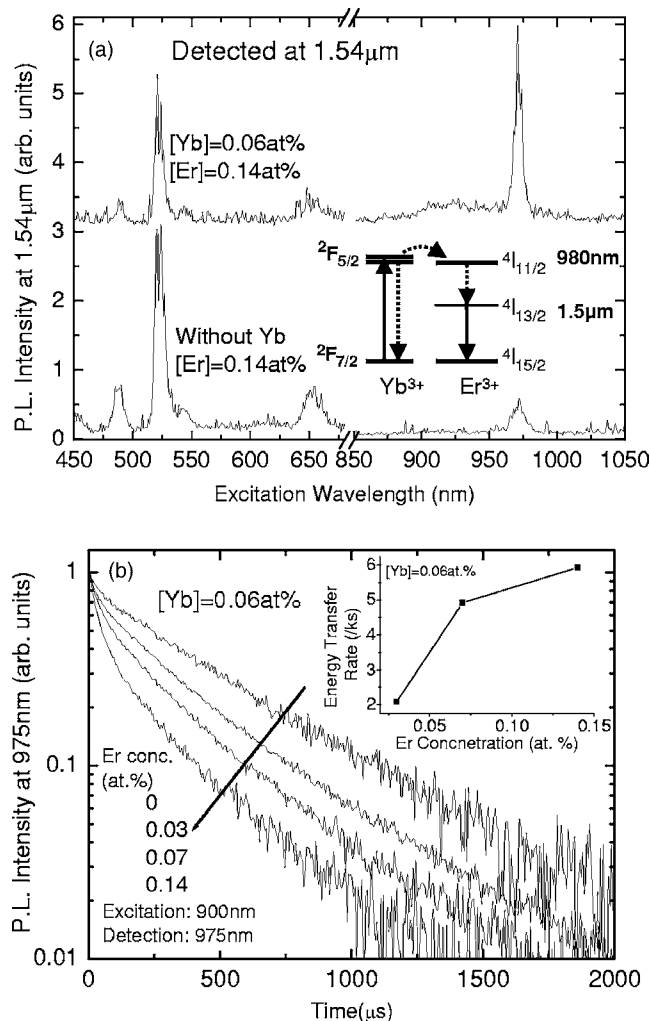


FIG. 1. (a) PLE spectra detected at  $1.54 \mu\text{m}$  for  $\text{Er:Yb:Al}_2\text{O}_3$  and  $\text{Er:Al}_2\text{O}_3$  samples. Er concentration is fixed to 0.14 at. %. Inset: schematic illustration of energy level diagrams of  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$ . (b) PL decay curves detected at 975 nm for the samples with different Er concentrations. The lifetimes estimated at the  $1/e$  of the intensity are 792, 298, 162, and 139  $\mu\text{s}$  for the Er concentrations of 0, 0.03, 0.07 and 0.14 at. %, respectively. Inset: energy transfer rate estimated from the shortening of the lifetime at 975 nm.

850 and 1000 nm.  $\text{Yb}^{3+}$  has an absorption peak at 980 nm and a broad absorption band in the range from 850 to 1000 nm.<sup>19</sup> Therefore, the enhancement of the excitation cross section in this wavelength range is due to indirect excitation of  $\text{Er}^{3+}$  to the second excited state by the energy transfer from  $\text{Yb}^{3+}$ . From the intensity ratio of  $\text{Er:Al}_2\text{O}_3$  and  $\text{Er:Yb:Al}_2\text{O}_3$  samples at 980 nm excitation,  $\text{Er}^{3+}$  in  $\text{Er:Yb:Al}_2\text{O}_3$  samples is excited mainly via  $\text{Yb}^{3+}$ .

The direct evidence of energy transfer from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  is obtained from the time transient of PL from  $\text{Yb}^{3+}$  at 980 nm. Figure 1(b) shows the PL decay curves at 975 nm for the samples containing 0.06 at. % of Yb and different amounts of Er. PL is excited at 900 nm, where  $\text{Er}^{3+}$  does not have any states and cannot be excited directly. Without Er doping, the decay curve is nearly a single exponential function and the decay time is 792  $\mu\text{s}$ . By Er doping, the decay curve deviates significantly from a single exponential function and the lifetime becomes shorter, which evidences non-radiative energy transfer from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$ . In a simplified model, where the shortening of lifetime is caused by the energy transfer to  $\text{Er}^{3+}$ , the relaxation rate of  $\text{Yb}^{3+}$  can be expressed as  $W_{\text{Yb,Er}} = W_{\text{Yb}} + W_{\text{ET}}$ , where  $W_{\text{Yb,Er}}$  and  $W_{\text{Yb}}$  are

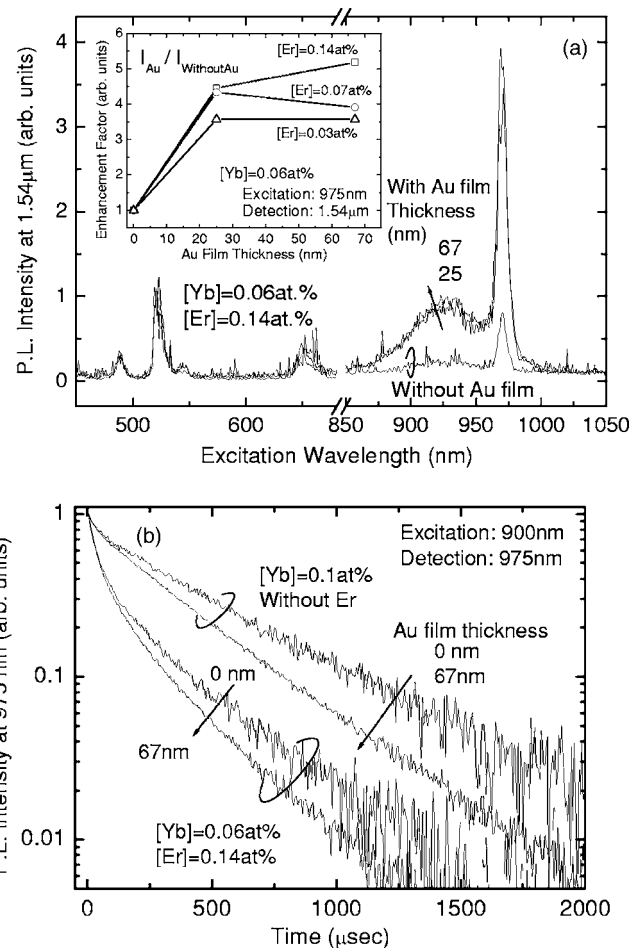


FIG. 2. (a) PLE spectra detected at  $1.54 \mu\text{m}$  for  $\text{Er:Yb:Al}_2\text{O}_3$  samples with and without a Au layer (25.0 or 67 nm) on top. Er and Yb concentrations are 0.14 and 0.06 at. %, respectively. Inset: enhancement factor of PL at  $1.54 \mu\text{m}$  as a function of Au thickness. The excitation energy is 975 nm. (b) PL decay curves detected at 975 nm for  $\text{Er:Yb:Al}_2\text{O}_3$  and  $\text{Yb:Al}_2\text{O}_3$  samples. The curves with and without a Au layer (67 nm) are compared.

measured decay rates of 975 nm emission of  $\text{Yb}^{3+}$  for  $\text{Er:Yb:Al}_2\text{O}_3$  and  $\text{Yb:Al}_2\text{O}_3$  samples, respectively, and  $W_{\text{ET}}$  is the energy transfer rate. We estimated the decay rates by fitting the decay curves by a stretched exponential function and extracted the energy transfer rate. The estimated energy transfer rates are plotted in the inset of Fig. 1(b). Since  $W_{\text{ET}}$  is proportional to the Yb–Er interaction coefficient and to Yb and Er concentrations, it becomes larger with increasing Er concentration.

It is worth noting that although  $\text{Er}^{3+}$  is not directly excited by 900 nm light, it can be excited by the energy transfer from  $\text{Yb}^{3+}$ , and the radiative transition from the second excited to the ground states of  $\text{Er}^{3+}$  can in principle contribute to the 980 nm PL. To estimate whether the contribution of  $\text{Er}^{3+}$  is negligibly small or not, we measured the decay curves of the PL at 975 nm for the samples not containing Yb by exciting  $\text{Er}^{3+}$  by 520 nm light. The measured lifetime was shorter than 20  $\mu\text{s}$ . This time is much shorter than those obtained in co-doped samples shown in Fig. 2. Furthermore, the intensities were much smaller. Therefore, the contribution of  $\text{Er}^{3+}$  to the 980 nm emission is negligibly small, and the observed shortening of the lifetime by Er doping is due to energy transfer to  $\text{Er}^{3+}$ .

Figure 2(a) shows PLE spectra detected at  $1.54 \mu\text{m}$  for  $\text{Er:Yb:Al}_2\text{O}_3$  samples with two different thicknesses of Au

layers on top. Er and Yb concentrations are fixed to be 0.14 and 0.06 at. %, respectively. In the excitation wavelength range between 450 and 680 nm, where Er is excited by direct photon absorption, no significant change is seen on the spectra. On the other hand, strong enhancement of the intensity is observed when the samples are excited by longer-wavelength light. In the inset of Fig. 2(a), PL intensity at 1.54  $\mu\text{m}$  excited by 975 nm light for Er: Yb:  $\text{Al}_2\text{O}_3$  samples with various Er concentrations are plotted as a function of the thickness of the Au layer. The intensity is normalized to that of the samples without Au layers. The vertical axis thus represents the “enhancement factor.” We can see strong enhancement for all the samples. No significant difference in the enhancement factor is seen between the Au thicknesses of 25 and 67 nm.

One of the possible mechanisms for the enhancement of the 1.54  $\mu\text{m}$  PL when excited at around 980 nm is that local electric field intensity of the incident light is enhanced due to the roughness on the Au layer; that is, surface plasmons propagating on the surface (or at the interface) are perturbed by the roughness and the perturbation allows the direct coupling of the plasmons with the incident light. The energy of the surface plasmon resonance depends strongly on the condition of the metal surface. In the present samples, we measured transmittance and reflectance of the Au films, and estimated the ratio of photons absorbed by the films. We found that the absorption due to surface plasmon resonances starts from about 850 nm for both the 25 and 67 nm Au films. Therefore, the observed strong PL enhancement when excited at around 980 nm and the lack of it when excited at 520 and 650 nm can be qualitatively explained by different degree of local field enhancement depending on the excitation wavelengths.

Another possible mechanism of the PL enhancement when excited at 980 nm is that the rate of energy transfer from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  is enhanced by the existence of the Au layer. In Fig. 2(b), the PL decay curves of  $\text{Yb}^{3+}$  detected at 980 nm for the samples with and without Au layers (67 nm) are compared. For the sample not containing Er, we can see the shortening of the lifetime. The shortening can be explained by two mechanisms.<sup>20</sup> The first one is the enhancement of radiative rate due to that of PMD. The other one is resonant coupling of excited  $\text{Yb}^{3+}$  with the surface plasmons and also the excitation of intra- and interband transitions of the Au layer. These couplings result in nonradiative energy transfer from  $\text{Yb}^{3+}$  to the Au layer, and thus the luminescence is quenched and the lifetime is shortened.

The shortening of lifetime can also be seen for Er and Yb co-doped samples. By the procedure mentioned earlier, we estimated the energy transfer rates for all series of samples. In Fig. 3, the energy transfer rates divided by those of the samples without Au layers are plotted as a function of the Au film thickness. We can see 50% to 80% increase of the energy transfer rate. The enhancement is considered to be due to that of PMD by placing the Au layer nearby the Yb–Er coupled systems. However, in order to discuss the effects more in detail and quantitatively, the dependence of the rate as a function of the distance between the active and Au layers should be studied. These experiments are now underway in our laboratory. In Fig. 3, the energy transfer rates do not depend strongly on Au thickness. It is of great interest to study much thinner island films, because the interaction

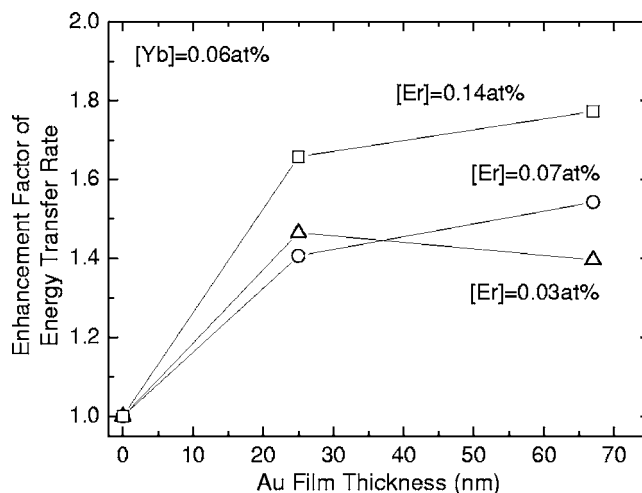


FIG. 3. Enhancement factor of the energy transfer rates as a function of Au film thickness for the samples with different Er concentrations.

between light and surface plasmons in islands is much different from that in continuous films.

In conclusion, we demonstrated that the 1.54  $\mu\text{m}$  emission from Er and Yb co-doped  $\text{Al}_2\text{O}_3$  films is strongly enhanced by just placing a thin Au layer on top when they are excited by near-infrared light. The enhancement is caused by the strong local electric fields accompanied by the excitation of surface plasmons in a rough metal surface. In addition, we demonstrated the enhancement of the energy transfer rate, which is probably due to the enhancement of PMD in the positions of Yb–Er coupled systems.

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