Extraordinary infrared photoluminescence efficiency of Er$_{0.1}$Yb$_{1.9}$SiO$_5$ films on SiO$_2$/Si substrates

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Extraordinary infrared photoluminescence efficiency was found for Er$_2$SiO$_5$ film by optimizing the composition of Yb additions on SiO$_2$/Si substrates. Above two orders of magnitude enhanced 1.53 μm Er$^{3+}$ photoluminescence for the Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film on SiO$_2$/Si substrate was obtained by pumping at 980 nm compared with pure Er$_2$SiO$_5$ film on Si substrate at 654 nm. All Er ions for Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film are optically active. The decreased nonradiative transient rate leads to extraordinary photoluminescence efficiency in the Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film. It indicated that the Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film is the sought candidate material for compact waveguide amplifiers and emitters in silicon photonics integration. © 2011 American Institute of Physics. [doi:10.1063/1.3554750]

Er silicates (Er$_2$SiO$_5$ and Er$_2$Si$_2$O$_7$) have been attracting considerable attention as Er based materials for small size and high optical gain light source in silicon photonics integration, since Er silicates contain a higher Er density of ~10$^{25}$ cm$^{-3}$ in contrast to Er doped Si-based materials ($10^{16}$–$10^{20}$ cm$^{-3}$). However, such a high concentration results in upconversion due to near distances of Er ions that limits the Er luminescence. Therefore, characterizing and controlling Er ions distances in such Er silicates are necessary. An effective strategy to reduce this upconversion is to add yttrium (Y) cations into the structure, where they substitute Er ions in the silicate lattice and prevent neighboring Er ions from causing upconversion due to similar ionic radius between Y and Er. Ytterbium (Yb) and Er also have similar ionic radius (Yb: 0.86 Å and Er: 0.89 Å). Meanwhile, it is very known that Yb, as an efficient sensitizer of Er$^{3+}$ at 980 nm excitation wavelength, can absorb more pump power than Er, leading to strong Er luminescence. However, little about Er–Yb silicates was reported. In addition, we have found that excess O on SiO$_2$ substrate has a significant effect on photoluminescence (PL) of Er silicate. Control of the quantity of Er, Si, and O has been found to be important to obtain highly crystalline Er silicates. In this paper, we reported extraordinary infrared photoluminescence efficiency of Er$_2$SiO$_5$, by optimizing the composition of Yb additions on SiO$_2$/Si substrates pumping at 980 nm compared with pure Er$_2$SiO$_5$ film on Si substrate at 654 nm, and discussed the responsible enhancement mechanism.

Er$_{2-x}$Yb$_x$SiO$_5$ (x = 0, 0.1, 0.2, 0.4, 1.0, 1.5, 1.9, 1.96) films were fabricated by using a mixture of Er–O, Yb–O, and Si–O ([Er+Yb]:Si = 2:1] sol solutions, respectively. The sol solutions were spin coated on SiO$_2$(600 nm)/Si(100) substrates and Si(100) substrates, dried at 150 °C for 30 min in air, and baked at 600 °C for 30 min in Ar. This coating and baking procedure was repeated five times to obtain about 360 nm thick preform films. Finally, each sample was covered with a Si wafer and sintered in a furnace at a high temperature of 1200 °C for 30 min, with a heating rate of 100 °C/min in Ar.

Phase structure of the samples was examined using a Rigaku x-ray diffractometer (XRD) with Cu Kα radiation. Photoluminescence measurements were performed by using two semiconductor laser diodes with a 100 mW power at 980 and 654 nm. This wavelength corresponds to the direct excitation of Er ions from $^4$I$_{15/2}$ to $^2$H$_{11/2}$, $^4$I$_{15/2}$, respectively. The PL emissions were collected and dispersed by an HR550 triple-grating monochrometer mounted with an electrically cooled InGaAs photodetector, and followed by a lock-in amplifier. A digital oscilloscope with a bandwidth of 100 MHz measured the fluorescent lifetimes.

Figure 1(a) shows the PL spectra of Er$_{2-x}$Yb$_x$SiO$_5$ (x = 0–2) films on Si(100) substrates at the wavelength pump of 654 nm. It can be seen that the typical PL spectrum with main peak at 1.528 μm of Er$_2$SiO$_5$ phase (JCPDS No. 52-1809) was observed without Yb additions (x = 0). The PL spectra have no significant change with the increase of Yb concentration to 2.5 at. % (x = 0.2) compared with that of Er$_2$SiO$_5$ phase. However, the peak intensity at 1.528 μm becomes weak, and another two strong peaks at 1.535 and 1.545 μm appear when the Yb concentration was further increased to above 12.5% (x = 1.0). It shows that the local environment of Er ions has been changed compared with that of samples having low Yb concentrations. The 1.53 μm integrated PL intensity is similar to the different Yb concentrations at 654 nm pump wavelength. In order to study the effect of Yb on Er, 980 nm wavelength laser was used as pump source. Figure 1(b) shows the 1.53 μm integrated PL intensity of Er$_{2-x}$Yb$_x$SiO$_5$ films on SiO$_2$/Si substrates and Si(100) substrates as a function of Yb concentration at 980 and 654 nm pump wavelengths. PL intensity by pumping at 980 nm has a significant increase than that by pumping at 654 nm. All Er ions for Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film is the sought candidate material for compact waveguide amplifiers and emitters in silicon photonics integration.

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for the Er$_{2-x}$Y$_x$SiO$_5$ ($x=1.9$) film on SiO$_2$/Si substrate was observed compared with that on the Si substrate by pumping at 980 nm.

Figure 2(a) shows the XRD patterns of Er$_{2-x}$Y$_x$SiO$_5$ ($x=0–2$) films on Si(100) substrates. The strong peaks of (100), (200), and (300) at 10.3°, 20.6°, and 31.2° from Er$_2$SiO$_5$ film (JCPDS 52-1809) were observed without Yb additions ($x=0$). With the increase of Yb concentration to 2.5 at. % ($x=0.2$), the XRD pattern has no significant change, indicating that the phase structures are similar to the samples with low Yb concentrations. However, the three strong peaks became blurred when the Yb concentration was increased to above 12.5 at. % ($x=1.0$). Another series of peaks appear and are completely consistent with another Er$_2$SiO$_5$ phase (JCPDS No. 40-0384). So it can be confirmed that one Er$_2$SiO$_5$ phase (JCPDS No. 52-1809) formed below the Yb concentration of 2.5 at. % ($x=0.2$), and another Er$_2$SiO$_5$ phase with monoclinic structure (JCPDS No. 40-0384) formed above the Yb concentration of 12.5 at. % ($x=1.0$). It can also explain the reason for PL shape change when the Yb concentration was increased to 12.5 at. % ($x=1.0$). The two strong peaks at 1.535 and 1.545 μm for the PL spectrum should come from another Er$_2$SiO$_5$ phase (JCPDS No. 40-0384). Figure 2(b) shows the XRD patterns of Er$_{2-x}$Y$_x$SiO$_5$ ($x=0–2$) films on SiO$_2$/Si substrates with the increase of Yb concentration from 12.5 at. % ($x=1.0$) to 24.5 at. % ($x=1.96$). The peak positions are consistent with that on the Si substrate, showing that the substrate has no evident effect on phase structure of Er$_{2-x}$Y$_x$SiO$_5$ films.

Figure 3 shows the decay time of Er$_x$Y$_{2-x}$SiO$_5$ ($x=0–2$) films on SiO$_2$/Si substrates and Si substrates. For pure Er$_2$SiO$_5$ phase on Si substrate, fast decay time of ~20 μs was observed. The slow decay time of ~0.7 ms was observed for Er$_x$Y$_{2-x}$SiO$_5$ films on SiO$_2$/Si substrate for high Yb concentration of 18.75 at. % ($x=1.5$). With the further increase of Yb concentration to 23.75 at. % ($x=1.9$) and 24.5 at. % ($x=1.96$), decay times become longer ~1.8 and ~3.5 ms, above 100 times of pure Er$_2$SiO$_5$. The smaller amount of Er and higher amount of O supplied from the SiO$_2$ underneath layer compared with Er$_2$SiO$_5$ may result in the longer decay time. The enhancement of decay time with increasing composition of Yb additions can be explained by the decrease in the number of nonradiative decay channels, which may involved reduction of concentration quenching of Er ions at high Yb concentrations. Energy transfers among Er ions, which may lead to a longer lifetime of Er ions, have been known to be effective in Er@core–Y@shell nanoparticles.14 In the Er@core–Y@shell nanoparticles, Er ions are able to give off their energy to Y ions, which stabilize Er ions and prolong their lifetimes.

FIG. 1. (a) PL spectra of Er$_{2-x}$Y$_x$SiO$_5$ ($x=0–2$) films on Si(100) substrates at the wavelength pump of 654 nm. (b) 1.53 μm integrated PL intensity of Er$_{2-x}$Y$_x$SiO$_5$ films on SiO$_2$/Si substrates and Si(100) substrates as a function of Yb concentration at 980 and 654 nm pump wavelengths.

FIG. 2. XRD patterns of Er$_{2-x}$Y$_x$SiO$_5$ films on (a) Si(100) substrates and (b) SiO$_2$/Si(100) substrates.

FIG. 3. Decay time of Er$_x$Y$_{2-x}$SiO$_5$ films on SiO$_2$/Si substrates and Si substrates.
Er ions become very efficient when the distances of neighboring Er ions get to be smaller. The energy finally dissipates to quenching centers such as –OH when they meet with an excited Er ion.

Above 200 times enhanced PL intensity was observed for the Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film on SiO$_2$/Si substrate by pumping at 980 nm compared with pure Er$_2$SiO$_5$ film on Si substrate at 654 nm. First, Yb ions have a larger optical cross section and can transfer energy to Er ions efficiently for 980 nm pump wavelength. The absorption curve of Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film was measured, and the absorption for 980 nm wavelength is about five times than that for 654 nm wavelength. In addition, a proper molar ratio of Yb and Er was needed to gain the maximum PL intensity. Dong et al. fabricated the Er–Yb doped Al$_2$O$_3$ materials and found that ratio of Yb and Er [(10–20):1] can get maximum PL efficiency. The sensitization effect was also observed in a series of the Er–Yb codoped phosphate glasses [LiEr$_x$Yb$_1$La$_{(1-x)}$P$_2$O$_{12}$] prepared using electronic furnace in a temperature of 1200–1300 °C by Zhang et al. The maximum PL intensity was observed when the molar ratio of Yb and Er is about 20:1. In addition, we considered decay time of the samples.

Photoluminescence intensity and lifetime are related to rate equations governing the excitation and decay of the Er ions,

$$I = \alpha \phi N \pi \tau_{\text{rad}},$$

where $\alpha$ is the excitation cross section, $\phi$ is the incident photon flux, $N$ is the optically active Er content, $\pi$ is the total lifetime, and $\tau_{\text{rad}}$ is the radiative lifetime. Therefore, using fixed $\alpha$, $N$, and $\tau_{\text{rad}}$ according to the above equation, PL intensity ($I$) can be explained by measuring $\pi$ for the two samples under the same excitation conditions. The lifetime $\pi$ for Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film is about 1.8 ms, about 100 times higher than 20 $\mu$s for Er$_2$SiO$_5$ as shown in Fig. 2. From Eq. (1), we can conclude that above two orders of magnitude enhanced PL for Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film may be due to the higher radiative transition rate. However, although decay time becomes longer about 3.5 ms for Er$_{0.04}$Yb$_{1.96}$SiO$_5$ film with the Yb concentration that further increased to 24.5 at. % ($x=1.96$), PL intensity decreases. First, we can assume that all Er ions are optically active for Er$_{0.04}$Yb$_{1.96}$SiO$_5$ film due to such low Er concentration (Er ions is 0.5 at. %). It is suggested that $\sigma$ and $\tau_{\text{rad}}$ for Er$_{0.1}$Yb$_{1.9}$SiO$_5$ and Er$_{0.04}$Yb$_{1.96}$SiO$_5$ are the same. So $N(x=1.9)$ = $N(x=1.96)$/$I(x=1.96)/I(x=1.9) = 1.26$ at. % according to the equation, which is quite consistent with a real Er concentration of 1.25 at. % for Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film. It can be concluded that all Er ions are optically active for Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film. It indicated the Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film is the sought candidate material for compact waveguide amplifiers and emitters in silicon photonics integration.

Above 200 times enhanced 1.53 $\mu$m Er$^{3+}$ photoluminescence intensity was observed for the Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film on SiO$_2$/Si substrate by pumping at 980 nm. Another Er$_2$SiO$_5$ phase with monoclinic structure (JCPDS No. 40-0384) was observed for high composition of Yb additions. The ratio of Yb and Er (19:1) for Er$_{2-x}$Yb$_x$SiO$_5$ films can get maximum PL efficiency. All Er ions for the Er$_{0.1}$Yb$_{1.9}$SiO$_5$ are optically active. The decreased nonradiative transient rate is the main reason for extraordinary infrared photoluminescence efficiency of Er$_{0.1}$Yb$_{1.9}$SiO$_5$ film on SiO$_2$/Si substrate.

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