Anneal temperature dependent Er$^{3+}$/Tm$^{3+}$ energy transfer and luminescence from Er and Tm co-doped silicon-rich silicon oxide

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A R T I C L E   I N F O

Article history:
Received 22 November 2009
Received in revised form 3 June 2010
Accepted 6 June 2010
Available online 14 June 2010

Keywords:
Silicon
Nanoclusters
Rare-earth doping
Photoluminescence
Erbium
Thulium
Plasma-enhanced chemical vapor deposition
Annealing

A B S T R A C T

The effect of the anneal temperature on the Er$^{3+}$/Tm$^{3+}$ energy transfer and subsequent Er$^{3+}$/Tm$^{3+}$ luminescence from Er/Tm co-doped, silicon-rich silicon oxide films are investigated. The anneal procedure necessary for optimum photoluminescence (PL) from the co-doped film is substantially different from that for only Er- or Tm-doped films. Analysis and modeling of PL intensity and time-resolved PL indicate that this higher optimum anneal temperature is due to the anneal temperature dependent Er–Tm interactions. In addition, the optimization of combined ultrabroad Er/Tm luminescence was discussed controlling Er–Tm interactions which is tailored by the change of Er/Tm doping ratio and anneal temperature.

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1. Introduction

Rare earth (RE) ions, when co-doped into a dielectric host material with nanocluster Si (nc-Si), can be excited non-resonantly through an Auger-like interaction with electrical carriers injected into the nc-Si[1–5]. This combines the large, broad absorption cross-section of nc-Si with the sharp, stable luminescence of RE ions, enabling low-cost pumping using visible light emitting diodes (LEDs) [6–9] as well as electrical excitation [10]. Furthermore, since such nc-Si sensitization of RE ions does not require resonant pump photons, different RE species can be simultaneously excited and luminescent, pumped by a single excitation source, in a single film doped with more than one RE ion specie. For example, Fig. 1 (a) shows the example of this excitation and luminescence process in Er- and Tm-doped nc-Si films. Pump photons generate excitons in nc-Si, as denoted with (i) in the figure. The exciton recombination energy is then transferred to both doped Er$^{3+}$ and Tm$^{3+}$ ions, exciting RE ions to higher 4f levels (denoted with (ii)), and excited RE ions radiatively decay, producing corresponding RE luminescences (denoted with (iii)). As a result, this combined luminescence of 1.54 μm Er$^{3+}$ (due to $^4I_{13/2}$→$^4I_{15/2}$) and 1.78 μm Tm$^{3+}$ (due to $^3F_4$→$^3H_6$ 4f transitions) is very wide, covering 1.5 to 1.9 μm [11].

This indicates that an ultra-wideband optical amplifier pumped with visible LEDs that can cover nearly the whole C- and L- or U-band of silica based optical fiber may be feasible [12]. Typically, nc-Si sensitization of RE ions including Er and Tm is achieved by annealing RE-doped silicon-rich silicon oxide (SRSO) at a high temperature to form nc-Si in silica matrix. For a SRSO film doped with single RE specie, it has been reported that the nc-Si sensitization can be optimized at certain anneal temperatures thanks to the results of the compromise mainly between the nc-Si formation and Er precipitation [13,14]. In the case of SRSO films doped with two different RE ions, on the other hand, the results of thermal treatment seem to be more difficult to predict because several distinct interactions between different RE species also exist simultaneously, in addition to nc-Si/RE ions interactions illustrated in Fig. 1 (a). As schematically explained in Fig. 1 (b), for Er/Tm co-doped films, the $^4I_{13/2}$→$^4I_{15/2}$ Er$^{3+}$ is nearly resonant with the $^3H_4$→$^3F_4$ Tm$^{3+}$ 4f transition. Thus an inter-RE up-conversion, referred to as (iv) in the figure, in which an excited Er$^{3+}$ ion decays non-radiatively by exciting an excited Tm$^{3+}$ ions from $^3F_4$ to $^3H_4$ state, is possible at a rate that can be as fast as ~3×10$^3$ s$^{-1}$ [11]. As the Tm$^{3+}$ ion then rapidly decays non-radiatively back to $^3H_4$ state, the result is a decrease of the Er$^{3+}$ luminescence intensity without a change in Tm$^{3+}$ luminescence. This Er–Tm interaction can be controlled by the atomic ratio or distance between the Er$^{3+}$ and Tm$^{3+}$ ions [15–17]. However thermal anneal can also lead to further variation of the Er–Tm energy transfer rate.
from that initially targeted, as different RE ions can be affected differently by the same anneal procedure.

Hence, for the optimization and further photonic application, the effect of thermal anneal on the combined Er/Tm luminescence from Er and Tm co-doped SRSO needs to be studied. In this paper, we report on the effect of the anneal temperature on the Er–Tm energy transfer and luminescence properties from Er and Tm co-doped SRSO. We find that the optimum luminescence from Er/Tm co-doped SRSO requires an anneal temperature that is substantially higher than that for SRSO doped with Er or Tm only. The analysis of both Er/Tm luminescence intensity and time-resolved luminescence decay traces as a function of anneal temperature indicates that the higher optimum anneal temperature for co-doped film is due to the relatively low Er–Tm energy transfer, which resulted from the differences in the anneal temperature dependence of nc-Si sensitized Er$^{3+}$ and Tm$^{3+}$ luminescence. An appropriate model was built to explain the anneal temperature dependent Er/Tm energy transfer rate and RE luminescence. The model was consistent with experimental data. Furthermore, the model could also predict the effect of anneal temperature on RE luminescence for the SRSO film doped with arbitrary Er/Tm concentrations. The results imply that interactions between different rare earth ions need to be taken into account in optimizing the design process for nc-Si sensitization of multiple rare-earth doped thin films.

2. Experiments

Er and Tm co-doped SRSO thin films were deposited on a Si [100] wafer by electron cyclotron resonance-plasma enhanced chemical vapor deposition of SiH$_4$ and O$_2$ with concurrent sputtering of Er and Tm target. By Rutherford backscattering spectroscopy and secondary ion mass spectroscopy, the film thickness, Si content, Er, and Tm content were found to be 1.4 μm, 35 at.%, 0.04 at.%, and 0.12 at.%, respectively. For comparison, SRSO thin films with similar thickness and excess Si content that were doped with Er or Tm only were also prepared. Henceforth, co-doped, Er-doped, and Tm-doped films will be referred to as ErTm, Er, and Tm films, respectively. After deposition, the films were isochronically annealed at different temperatures (700–1250 °C) for 30 min. Afterward, the films were hydrogenated by anneal at 700 °C for 1 h in flowing H$_2$ forming gas for nc-Si passivation. Photoluminescence (PL) spectra were measured using the unfocused 488 nm line of an Ar laser, a long-wavelength enhanced InGaAs PIN photodiode, and the lock-in technique, at room-temperature. The nominal pump power was 500 mW. Even though the 488 nm line can be resonantly absorbed by Er$^{3+}$, RE$^{3+}$ ions in SRSO are thought to be excited and luminescent mainly via the energy transfer from nc-Si not via direct resonant excitation of RE ions due to a high absorption cross-section of nc-Si than that of Er$^{3+}$ for 488 nm photons. Time-resolved Er$^{3+}$ or Tm$^{3+}$ PL decay traces were measured with a digitizing oscilloscope. Spectra were corrected according to the system spectral response. The time system response was 0.18 ms.

3. Results

Fig. 2 shows PL spectra from Er and Tm films that were annealed at 700, 950, and 1250 °C. We observed typical 1.54 μm Er$^{3+}$ luminescence due to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition and broad infrared luminescence, peaked at $\lambda = 1.75$ μm due to the Tm$^{3+}$ $^3F_4 \rightarrow ^2F_4$ transition. The inset of Fig. 2 summarizes the effect of anneal temperature on the integrated Er$^{3+}$ and Tm$^{3+}$ intensity for Er and Tm, respectively. Solid lines of the inset are a guide for the eyes produced by Gaussian fits of experimental results. Both Er$^{3+}$ and Tm$^{3+}$ luminescence intensities increased as the anneal temperature was increased to 850–950 °C, and were then quenched by more than an order of magnitude after the 1250 °C anneal. When compared to Er films, Tm films generally display stronger integrated RE luminescence. Note, however, that the Tm$^{3+}$ PL intensity starts to decrease at a lower anneal temperature than the Er$^{3+}$ PL intensity does, and becomes nearly completely quenched after the 1250 °C anneal.

Such anneal temperature dependence of RE luminescence of RE doped SRSO films has been widely reported, and is the combined result of the RE ion activation and nc-Si formation induced by the thermal anneal [13]. Thermal treatments are crucial for the optical activation of RE ions by removing defects in the as-deposited films, but further higher temperature anneal at temperatures greater than 1000 °C can lead to RE clustering and subsequent optical de-activation [18,19] as well as breaking of the coupling between nc-Si and RE ions [20]. In addition, the nc-Si formation of the Si-SiO$_2$ phase separation occurs at lower anneal temperatures, but further growth and crystallization of nc-Si at higher temperatures are not favorable any longer for the efficient RE luminescence due to the lower bandgap of large crystalline nc-Si [14]. As a result, RE luminescence was optimized at a certain anneal temperature, where all contributing factors are balanced, as shown in Fig. 2.

In the case of ErTm film, we observed a broad 1.4–2.0 μm luminescence peak which is comprised of Er$^{3+}$ and Tm$^{3+}$ luminescence. The inset of Fig. 3 summarizes the effect of anneal temperature on the integrated Er$^{3+}$ and Tm$^{3+}$ luminescence intensity for the ErTm film. We found that the effect of anneal temperature on the Tm$^{3+}$ luminescence was separated from the broader Er$^{3+}$ luminescence peak which is comprised of Er$^{3+}$ and Tm$^{3+}$ luminescence, as shown in Fig. 3. In order to investigate the individual RE luminescence, the Er$^{3+}$ luminescence peak was separated from the broader Tm$^{3+}$ luminescence by the interpolation of Tm$^{3+}$ luminescence in the range of 1.45–1.6 μm. We found that the effect of anneal temperature on the Tm$^{3+}$ luminescence intensity from the ErTm film is nearly the same as that on the Tm film. However, the effect of anneal temperature on the Er$^{3+}$ PL intensity from ErTm films is very different from that on the Er film. The Er$^{3+}$ PL intensity from the ErTm films remains very small in the anneal temperature range of 700–950 °C, and has a sharp maximum in the 1050–1150 °C range.

![Fig. 1.](Image 64x575 to 272x741) The schematic description of energy diagram of Si-nc, Er$^{3+}$, and Tm$^{3+}$.

(a) excitation and luminescence of Er$^{3+}$ and Tm$^{3+}$ by energy transfer from Si-nc, and (b) additional energy transfer from Er$^{3+}$ to Tm$^{3+}$.

![Fig. 2.](Image 340x83 to 533x222) (Color online) Infrared photoluminescence spectra for Er-doped and Tm-doped films annealed at 700, 950, and 1250 °C. The inset summarizes integrated Er$^{3+}$ PL of Er film and Tm$^{3+}$ PL of film as a function of anneal temperature.
Given the similar effect of anneal temperature on the Er$^{3+}$ and Tm$^{3+}$ PL intensities from Er and Tm films, respectively, the reason why there would be such a sharp difference between the effect of anneal temperature on the Er$^{3+}$ and Tm$^{3+}$ PL intensities from Er/Tm films is not obvious. Thus, time-resolved Er$^{3+}$/Tm$^{3+}$ PL decay traces were analyzed for further insight. As the signal at 1.54 μm from Er/Tm films contains contributions from both Er$^{3+}$ and Tm$^{3+}$ ions, we can write

\[ \frac{dI_{\text{Er/Tm}}}{dt} = \frac{dI_{\text{Er}}}{dt} + \frac{dI_{\text{Tm}}}{dt} \]

where, \( \frac{dI_{\text{Er/Tm}}}{dt} \) and \( \frac{dI_{\text{Er}}}{dt} \) are relative steady state 1.54 μm PL intensity due to Er$^{3+}$ and Tm$^{3+}$ in Er/Tm films, respectively. In the case of the Er and Tm films, the RE luminescence decay can be described well with a single-exponential decay. However, in the case of the Er/Tm films, the RE luminescence decay cannot be described as a simple double exponential due to Er–Tm energy transfer that depends on the actual, time-varying concentration of excited Er$^{3+}$ and Tm$^{3+}$ ions. At the luminescence wavelength of 1.54 μm, the contribution by Tm$^{3+}$ is simple, as the Tm$^{3+}$ PL decay remains single-exponential. The contribution by Er$^{3+}$, on the other hand, is rather complicated because there are additional non-radiative decay paths for excited Er$^{3+}$ ions in Er/Tm films caused by Er–Tm interaction. Previously, we have shown that the time-resolved luminescence decay can then be written as [11,15]:

\[ \frac{dI_{\text{Er/Tm}}}{dt} = \frac{dI_{\text{Er}}}{dt} \exp(-W_{\text{Er}t}) + \frac{dI_{\text{Tm}}}{dt} \exp(-W_{\text{Tm}t}) \]

where, \( W_{\text{Er}t} \) and \( W_{\text{Tm}t} \) are the intrinsic decay rates of Er$^{3+}$ and Tm$^{3+}$ ions, and can be experimentally measured Er and Tm films, respectively. The symbol \( \alpha \) is the Er$^{3+}$ → Tm$^{3+}$ energy transfer rate, which is proportional to the coupling coefficient between Er/Tm ions and the number of excited Tm$^{3+}$ ions at steady state [11]. Using Eqs. (1) and (2), we can fit the 1.54 μm PL decay traces of Er/Tm films using only \( \alpha \) as the fitting parameter. In fitting the data, the relative ratio of \( \frac{dI_{\text{Er/Tm}}}{dt} \) to \( \frac{dI_{\text{Er}}}{dt} \) at time zero (0) was obtained using the relative steady state Er$^{3+}$ and Tm$^{3+}$ PL intensities at 1.54 μm obtained by interpolation of Tm$^{3+}$ luminescence in the range of 1.45–1.60 μm. The results for the values of \( \alpha \) as a function of anneal temperature, found by the fit, are shown as symbols in Fig. 4(a). We found that the value decreases nearly threefold from 1.0×10$^4$ to 3×10$^3$ s$^{-1}$ by increasing the anneal temperature from 700 to 1250 °C, indicating a corresponding decrease in the Er–Tm energy transfer at higher anneal temperatures. As the Er$^{3+}$→Tm$^{3+}$ energy transfer occurs via resonant dipole–dipole interactions [15,21], the physical mechanism behind the energy transfer is not expected to depend on the anneal temperature. Thus, the above decrease in the energy transfer rate is most likely due to the changing concentrations of excited Er$^{3+}$ and Tm$^{3+}$ ions. As Tm$^{3+}$ PL intensity starts to become quenched at lower anneal temperatures as shown in Fig. 3, we expect that a ‘single’ excited Er$^{3+}$ ion will encounter relatively less excited Tm$^{3+}$ ions that can lead to cooperative up-conversion as anneal temperatures increase, resulting in increased Er$^{3+}$ PL intensity. This is confirmed in Fig. 4(a) that shows the ratio of \( \frac{dI_{\text{Er/Tm}}}{dt} \) to \( \frac{dI_{\text{Er}}}{dt} \). We found that the effect of anneal temperature on the energy transfer rate \( \alpha \) agrees quite well with the effect of anneal temperature on the \( \frac{dI_{\text{Er/Tm}}}{dt} \) to \( \frac{dI_{\text{Er}}}{dt} \) ratio, confirming that the decrease in the Er–Tm energy transfer rate with increased anneal temperature is mostly due to the relatively stronger decrease in the excited Tm$^{3+}$ ion concentration at higher temperatures.

Further confirmation of the importance of the anneal-induced change of the RE luminescence plays in determining the anneal-induced decrease in the Er–Tm energy transfer rate can be found by the anneal temperature dependence of the Er$^{3+}$ PL intensity from the Er/Tm films. For Er films, in which the Er–Tm interaction is absent, Er$^{3+}$ PL intensity \( \frac{dI_{\text{Er}}}{dt} \) at steady state can be written as:

\[ \frac{dI_{\text{Er}}}{dt} = kN_{\text{Er}}W_{\text{Er}}G_{\text{Er}} \frac{G_{\text{Tm}}}{G_{\text{Er}} + W_{\text{Er}}} \]

where, \( K_{\text{Er}}, W_{\text{Er}}, \) and \( G_{\text{Er}} \) are the proportional factor, the optically active Er number, the radiative decay rate, and the generation rate, respectively. While the number of optically active Er ions is determined by the anneal temperature, the other parameters in Eq. (3) do not seem to be directly related with the anneal temperature. However, thermal anneal leads to the modification of the of SiO$_2$ matrix and nc-Si characteristics which are closely correlated with the parameters in the rate equation, and all parameters in Eq. (3) are thus assumed to be dependent on the anneal temperature. The values of \( W_{\text{Er}} \) can be directly measured from time-resolved PL intensity decay traces, and \( G_{\text{Er}} \) can be obtained using the relative steady state Er$^{3+}$ and Tm$^{3+}$ PL intensities from Er/Tm films that contain Tm$^{3+}$ ions except for the Er–Tm energy transfer, the anneal temperature dependent Er$^{3+}$ PL intensity for Er/Tm films can be calculated just by substituting \( W_{\text{Er}} \) by \( W_{\text{Er}} + \alpha \) in Eq. (3), giving us:

\[ \frac{dI_{\text{Er}}}{dt} = kN_{\text{Er}}W_{\text{Er}}G_{\text{Er}} \frac{G_{\text{Tm}}}{G_{\text{Er}} + W_{\text{Er}} + \alpha} \]

Again, all parameters in Eq. (4) were already found from experiments on the Er and Tm films, and \( \frac{dI_{\text{Er/Tm}}}{dt} \) is therefore easily evaluated. Fig. 4 (b) is the comparison between experimental results (symbols) which were already given in the inset of Fig. 3, and simulated results (solid line) of \( \frac{dI_{\text{Er/Tm}}}{dt} \) by Eq. (4). Even though Eq. (4) does not have any adjustable parameters at all, we find that it can describe the anneal temperature dependence of the Er$^{3+}$ PL intensity from Er/Tm films quite well, agreeing within 60% of the absolute values, and reproducing all the relevant factors, such as nearly constant Er$^{3+}$ PL intensity in the 700–900 °C range with the maximum at 1150 °C.

### 4. Discussion

Taken together, the data can be summarized to consistently indicate that in the case of Er/Tm film which contains both Er$^{3+}$ and Tm$^{3+}$ ions, energy transfer between the Er$^{3+}$ and Tm$^{3+}$ ions plays a more important role in determining the Er$^{3+}$ luminescence properties than the energy transfer between nc-Si and Er. This is surprising, given the reported strong nc-Si/RE energy transfer as fast as 10$^9$–10$^{10}$ s$^{-1}$ [4,22]. On the other hand, the reported interaction distance between amorphous nc-Si and Er is only 1 nm or less [22–24], while the Er–Tm interaction distance can be as large as several tens of nanometer [15]. Furthermore, for our films, the Tm$^{3+}$ ions concentration is 3 times higher, and the nc-Si concentration is however 10$^3$ times less than the Er$^{3+}$ concentration [5]. Therefore stronger Er–Tm interaction is attributed to their longer range interaction and higher Tm concentration. Hence, in order to improve RE luminescence, higher nc-Si density seems to be favorable, as the known approach to more efficient sensitization of RE [24]. In addition, the control of relative

![Fig. 3. (Color online) Infrared PL spectra of Er/Tm films annealed at different temperatures. The inset shows integrated Er$^{3+}$ and Tm$^{3+}$ PL as a function of anneal temperature.](image-url)
Er/Tm doping concentration can engineer the Er–Tm interaction. For example, when the Tm:Er doping ratio is reduced to 1:9 from the current ratio, another calculation reveals that the value of $a$ can be reduced to a few s$^{-1}$. And for such doping ratios, the optimum anneal temperature was found to be $\sim 1000$ °C which is also moderate for Tm luminescence resulting in optimized broad 1.4–1.9 µm Er/Tm combined luminescence.

5. Conclusion

In conclusion, we have investigated the effect of anneal temperature on the Er–Tm energy transfer and luminescence properties from Er and Tm co-doped SRSO. The required anneal temperature for optimum RE luminescence of Er/Tm co-doped SRSO is rather unique and higher than that for SRSO doped with Er or Tm only, due to the anneal temperature dependent Er–Tm interaction. The discrepancy in the anneal temperature dependence of excited Er$^{3+}$ and Tm$^{3+}$ numbers caused a single excited Er$^{3+}$ ion to encounter different Tm$^{3+}$ numbers and corresponding Er–Tm interaction strength. For nc-Si co-doped with multiple RE ions, together with nc-Si density and relative Er/Tm doping ratio, the effect of the anneal temperature on the Er–Tm interaction must also be taken into consideration for understanding and controlling the combined Er/Tm luminescence.

Acknowledgement

This work was supported by the New & Renewable Energy R&D program under the Ministry of Knowledge and Economy (MKE), Korea, and by the Korea Science and Engineering Foundation (KOSEF) (grant No. R01-2007-000-21036-0), and by the WCU Program by KOSEF (R31-2008-000-10071-0).

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Fig. 4. (Color online) (a) Symbols show the values of $a$ as a function of anneal temperature deduced from Eqs. (1) and (2) and line shows the values of relative intensity of Tm$^{3+}$ PL of Tm film compared to Er$^{3+}$ PL of Er film. (b) The comparison of $T$ dependent Er$^{3+}$ PL intensity of Er/Tm film between experimentally measured (symbols) and numerically predicted using Eqs. (3) and (4) (broken line).