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Comparison of the room temperature 1.53 μm Er photoluminescence from flash lamp and furnace annealed Er-doped Ge-rich SiO_2 layers

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The furnace and flash-lamp annealing (FLA) temperature dependent variation in the room temperature 1.53 μm Er photoluminescence (PL) from Er-doped Ge-rich SiO_2 layers is investigated. The appearance of the 1.53 μm Er PL is discussed in the framework of the phonon-assisted fluorescent resonant energy transfer from Ge-related luminescence-centers (LCs) to the Er^{3+} . Detailed analyses suggest that in case of FLA the decrease in the 1.53 μm Er PL intensity is governed by the temperature dependent recrystallization of Ge nanoclusters, while for furnace-annealing it is associated with the reduction in the LC- Er^{3+} coupling due to Ge out-diffusion and the formation of Er-rich clusters with increasing temperature. © 2010 American Institute of Physics. [doi:10.1063/1.3437652]

I. INTRODUCTION

Annealing is an inevitable step to activate rare-earth (RE) ions when introduced in a SiO_2 layer either by deposition or by ion implantation technique. Although the RE doped metal-oxide semiconductor light emitting devices have been investigated extensively,^{1,2} the efficiency is far from practical application mainly due to the formation of RE-rich clusters during the annealing treatment. The situation has improved significantly for Er-doped SiO_2 in presence of semiconductor nanocrystals (NCs).³ For instance, the Er^{3+} ions which are situated near semiconductor NCs can take part in an *energy transfer* process during optical or electrical pumping.^{3–5} They can also make a shell like structure around Ge NC core and undertake an *inverse energy transfer process* during electroluminescence (EL) studies.⁶ This process deteriorates due to the formation of Er-rich clusters by degrading the Ge NCs with increasing Er doping⁷ or by increasing out-diffusion of Ge toward the Si/ SiO_2 interface during furnace-annealing (FA).⁸ Furthermore, we have recently demonstrated that the Er-doped amorphized Ge nanoclusters can be recrystallized in absence of Ge out-diffusion during flash-lamp annealing (FLA) (Ref. 9) which commonly relies on an extremely short temperature pulse (generally in the millisecond range¹⁰). As a result, it enhances the inverse energy transfer process and so the 400 nm EL yield.⁹ In this article, we evaluate the FA and FLA temperature dependent variation in the 1.53 μm Er photoluminescence (PL) from Er-doped Ge-rich SiO_2 layers in the range of 800–1100 °C and illustrate the involved mechanisms based on time-resolved PL dynamics.

II. EXPERIMENTAL

Initially, 130 keV Ge ions were implanted with a dose of $4 \times 10^{16} \text{ cm}^{-2}$, which gives 7.4% Ge at the mean projected range R_p of $\sim 112 \text{ nm}$ (derived from the SRIM-2006

calculations¹¹) in a 200 nm thick thermally grown SiO_2 layer on *n*-type Si(100) wafers. Whereas one set of samples was furnace annealed at 950 °C for 60 min, the other one was subjected to FLA for 20 ms at 1050 °C with an additional preheating at ~ 700 °C to produce Ge NCs. Subsequently, 250 keV Er ions were implanted with a maximum concentration of 0.5% at $R_p \sim 115 \text{ nm}$, followed by FA at 800–1100 °C for 30 min (for the first set) and by FLA at 800–1100 °C for 20 ms (for the second set) to remove implantation-induced defects and to activate Er^{3+} ions. The Ge and Er concentrations at R_p were verified by Rutherford backscattering spectrometry with a 1.4 MeV $^4\text{He}^+$ beam. Cross-sectional transmission-electron-microscopy (XTEM) images were taken by a FEI Titan 80–300 S/TEM instrument operating at 300 keV. All the PL spectra were recorded at room temperature (RT) when excited with the 532 nm line of a 200 mW neodymium-doped yttrium aluminum garnet laser. The PL signals were analyzed with a single grating monochromator and detected by an InGaAs detector in the near infrared region with a standard lock-in technique, while the laser beam was modulated with a rotating chopper. The InGaAs detector was further employed to examine the time-resolved PL dynamics in combination with a photon counting system.

III. RESULTS AND DISCUSSION

The RT PL spectra of the flash lamp and the furnace annealed samples are exhibited in Figs. 1(a) and 1(b), respectively, in the range of 800–1100 °C. Although in any case the 1.53 μm Er PL intensity decreases with increasing annealing temperature, the effect is more pronounced in furnace annealed samples. An almost fourfold decrease of the 1.53 μm Er PL intensity can be discerned [see Fig. 1(b)] when the FA temperature increases from 800 to 1100 °C. Clearly, 800 °C FA gives the highest 1.53 μm Er PL intensity, which is also more than double than that for 800 °C FLA. For in-depth understanding, the decay time (τ) of the prominent 1.53 μm Er peak was estimated for each sample

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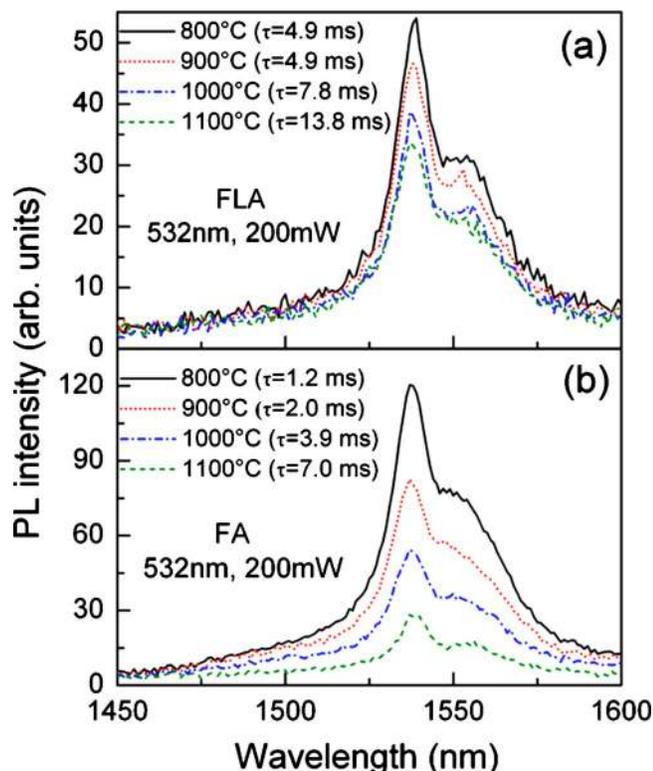


FIG. 1. (Color online) The RT PL spectra of 7.4%Ge+0.5%Er when flash lamp (a) and furnace (b) annealed with temperatures of 800 °C (solid curves), 900 °C (dotted curves), 1000 °C (dashed-dotted curves), and 1100 °C (dashed curves) for 20 ms and 30 min, respectively, after Er doping. In the corresponding legends, the decay time for each curve at the 1.53 μm Er peak position is depicted in parenthesis.

using a single exponential function [legends of Figs. 1(a) and 1(b)], showing in both cases τ is increasing with increasing annealing temperature. One can see that the τ values for the furnace annealed samples are always lower than that of the respective FLA ones.

The coexistence of the short-range Auger process and the Förster mechanism has been predicted behind the energy transfer process from Si NCs to the Er^{3+} ions.¹² On the other hand, the 1.53 μm Er PL from an Er-doped Ge-rich SiO_2 layer has recently been explained in the framework of a phonon-assisted fluorescent resonant energy transfer (FRET) to the Er^{3+} ions from Ge-related luminescence centers (LCs), which are increased with increasing amorphized Ge clusters by Er doping.¹³ In order to figure out the reason behind the annealing temperature dependent variation in the 1.53 μm Er PL intensity (Fig. 1), it is now important to follow the corresponding microstructure.

In case of flash lamp annealed samples and in absence of any Ge out-diffusion the density of Ge NCs was found to increase steadily with increasing FLA temperature from 800 to 1100 °C in Er-doped Ge-rich SiO_2 layers, whereas, the Ge NC size does not change very much.⁹ In fact, recent EL measurements confirm an increasing coupling of the Er^{3+} to the recrystallized Ge clusters with increasing FLA temperature, while the Er^{3+} ions that are staying apart from Ge clusters remain similar in all cases.⁹ Since the FRET depends on the LC- Er^{3+} intermediate distance, it has been demonstrated that this process can only dominate if the Er^{3+} ions reside

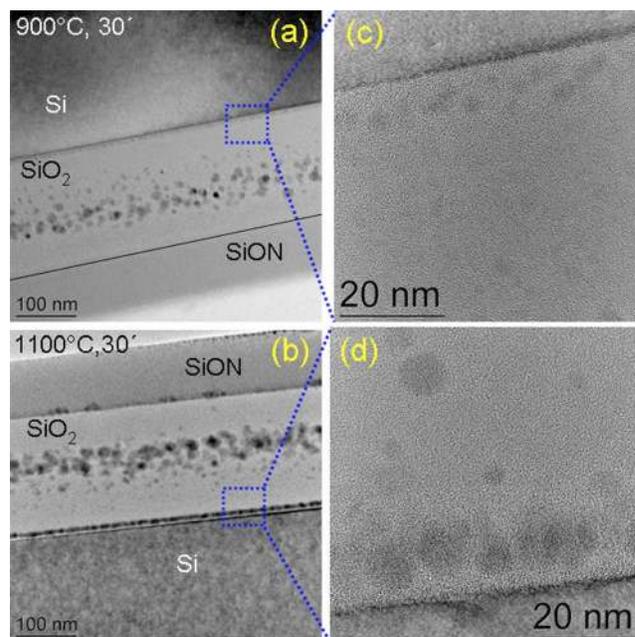


FIG. 2. (Color online) The XTEM images of 7.4%Ge+0.5%Er when furnace annealed with temperatures of 900 °C (a) and 1100 °C (b). The high-resolution images of the respective Si/ SiO_2 interfaces (marked by dashed boxes) are exhibited in (c) and (d). For clarity a line drawn in (a) to indicate the SiO_2/SiON interface.

within ~ 5 nm from the LCs, provided they are not attached to Ge NCs.¹³ Indeed, the latter one is a precondition for an inverse energy transfer process during EL studies.⁶ Based on EL results the observed decrease in the 1.53 μm Er PL intensity as a function of FLA temperature can be attributed to the decrease in the LC- Er^{3+} coupling due to a systematic loss of LCs with increasing recrystallization of the Ge clusters.⁹

In contrary, in addition to the Ge out-diffusion toward the Si/ SiO_2 and $\text{SiO}_2/\text{Si-oxynitride}$ (SiON) interfaces a phase transformation from the Er_2O_3 to $\text{Er}_2\text{Ge}_2\text{O}_7$ was observed with increasing temperature in case of FA.⁸ Beside Ge out-diffusion, the average size of Ge NCs in the central part of the SiO_2 layer was found to increase gradually with increasing FA temperature from 900 to 1100 °C [Figs. 2(a) and 2(b)]. The corresponding high-resolution XTEM images [Figs. 2(c) and 2(d)] near the respective Si/ SiO_2 interfaces (marked by dashed boxes) confirm that the segregated Ge atoms are not diffused in Si or form a wetting layer on Si during FA; instead a band of Ge NCs is formed and separated by a thin SiO_2 layer from the Si substrate. These observations suggest that their optical properties are mainly associated with the impurities (Ge and Er) embedded in the SiO_2 layer. Using EL measurements we have demonstrated that the Er segregates from Ge NCs and form Er-rich clusters with increasing FA temperature.⁸ Moreover, since the surface-to-volume ratio of Ge NCs is decreasing with increasing FA temperature, the number of Ge-related LCs at the Ge nanocluster surface will also be reduced with increasing average size of Ge NCs. Clearly, the probability to have the LC- Er^{3+} coupling will be reduced due to the loss of LCs and the Er clustering with increasing FA temperature resulting the observed PL quenching.

Small Si NCs are known to be suitable for a dominant

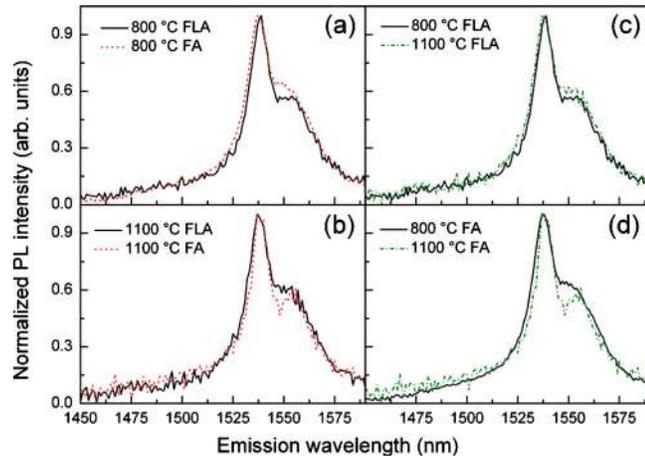


FIG. 3. (Color online) Comparison of the normalized RT PL spectra between 800 °C FLA and 800 °C FA (a), 1100 °C FLA and 1100 °C FA (b), 800 °C FLA and 1100 °C FLA (c), and between 800 °C FA and 1100 °C FA (d).

Auger-type energy transfer process to the Er^{3+} and for achieving sharp and intense $1.53 \mu\text{m}$ Er PL.¹² However, in case of Ge NCs the $1.53 \mu\text{m}$ Er PL intensity with smaller Ge NCs ($\sim 4 \text{ nm}$) in 800 °C FLA is found to be almost half than that for relatively bigger Ge NCs ($\sim 9 \text{ nm}$) in 800 °C FA. To understand the LC- Er^{3+} coupling, we compare the normalized $1.53 \mu\text{m}$ Er PL at the 800 and 1100 °C for FLA and FA (Fig. 3). As the Stark-splitting of the ground and first excited levels of Er^{3+} increases with increasing size of semiconductor NCs it will dominate in FA [Figs. 3(a), 3(b), and 3(d)]. Conversely, the spectral shape does not vary much with increasing FLA temperature [Fig. 3(c)] in accordance with the insignificant change in Ge NC size.⁹ Based on the above discussion it appears that compared to the samples of 800 °C FA, the decrease in the $1.53 \mu\text{m}$ Er PL intensity and the increase in τ by a factor of ~ 2 and ~ 4 , respectively, for 800 °C FLA cannot be explained in the light of Ge NC's size. It seems that the $1.53 \mu\text{m}$ Er PL is quenched by the remaining residual defects for 800 °C FLA. Indeed, the Er clustering with increasing FA temperature⁸ induces interaction between Er ions, which should decrease the τ values. However, the observed τ dependence implies that the decrease in nonradiative decay channels gives the major contribution in each set. For Er-doped Si-rich SiO_2 it is known that larger Si NC cause a stronger decrease in τ of the Er PL than smaller ones.¹² This effect which was explained by a higher density of photonic states in the vicinity of the NC (Ref. 14) may cause a higher radiative transition rate and thus a shorter decay time for excited Er^{3+} ions in the vicinity of larger Ge NCs. Consequently, τ is shorter for FA with larger Ge NCs compared to FLA at the same annealing temperature.

IV. CONCLUSIONS

In summary, we show the variation in the $1.53 \mu\text{m}$ Er PL intensity at RT with increasing FLA and FA temperature from 800 to 1100 °C. In particular, we demonstrate that the $1.53 \mu\text{m}$ Er PL intensity in any case decreases monotonically with a subsequent increase in τ by increasing annealing temperature. Although the annealing temperature dependent change in the $1.53 \mu\text{m}$ Er PL is prominent for furnace annealed samples, the maximum PL intensity obtained at 800 °C is almost double for furnace annealed sample than that of flash lamp one. Detailed microstructure and the PL analyses suggest that in absence of Ge out-diffusion, the reduction in the LCs due to recrystallization of Ge clusters with increasing FLA temperature decreases the phonon-assisted FRET from the LC to the Er^{3+} ions. Conversely, FA induced strong out-diffusion of Ge in parallel to the formation of Er-rich clusters and bigger Ge NCs in the central part of the SiO_2 layer reduces the LC- Er^{3+} coupling. Finally, the increase in τ in any case is discussed in the light of a decrease in nonradiative channels with increasing annealing temperature.

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