The Nd-nanocluster coupling strength and its effect in excitation/de-excitation of \( \text{Nd}^{3+} \) luminescence in Nd-doped silicon-rich silicon oxide

Se-Young Seo, a) Mun-Jun Kim, and Jung H. Shin

Department of Physics, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Kusung-dong, Yusung-gu, Taegon, Korea

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The Nd-nanocluster Si (nc-Si) coupling strength and its effect in excitation/de-excitation of \( \text{Nd}^{3+} \) luminescence in Nd-doped silicon-rich silicon oxide (SRSO) is investigated. Nd-doped SRSO thin films, which consist of nc-Si embedded inside a \( \text{SiO}_2 \) matrix, were prepared by electron-cyclotron-resonance plasma-enhanced chemical vapor deposition of \( \text{SiH}_4 \) and \( \text{O}_2 \) with cosputtering of Nd and subsequent anneal at 950°C. Efficient \( \text{Nd}^{3+} \) luminescence with moderate temperature quenching is observed. Based on an analysis of the temperature dependence of \( \text{Nd}^{3+} \) luminescence lifetime, we find a coupling strength between nc-Si and Nd that is strong enough to result in efficient excitation of \( \text{Nd}^{3+} \) via quantum-confined excitons, while weak enough to result in a small back-transfer rate is identified as the key to \( \text{Nd}^{3+} \) luminescence. © 2003 American Institute of Physics. [DOI: 10.1063/1.1615837]

Rare-earth (RE) doping of silicon has gathered much attention as a possible way of realizing a Si-based photonic material that can enable Si-compatible microphotonics. In particular, RE doping of silicon-rich silicon oxide (SRSO) that consists of nanocluster Si (nc-Si) embedded inside an \( \text{SiO}_2 \) matrix has proven successful in obtaining efficient RE luminescence. By now, luminescence from many different RE ions has been observed, and the possibility of optical gain from Er-doped nc-Si has been demonstrated.

While the exact details are not yet known, many results suggest that the exciton-mediated excitation mechanism originally proposed for RE ions in bulk semiconductors applies to RE ions in SRSO as well. That is, photogenerated free carriers in nc-Si form excitons that recombine by Auger-exciting the RE ions. A schematic description of this exciton-mediated excitation mechanism is given in Fig. 1. However, such excited RE ions can, with help of phonons, decay non-radiatively by creating an exciton. This process, labeled “back-transfer” in Fig. 1, has been identified to be a major factor contributing to the temperature quenching of RE luminescence that has plagued many RE-doped semiconductors.

One proven method to suppress back-transfer is using a wide-band-gap host material. A wide band gap tends to increase \( E_0 \), the energy mismatch between the exciton recombination energy and the RE intra-4f transition energy (See Fig. 1), thereby increasing the energy barrier against back-transfer. Alternatively, the band gap of a narrow-bandgap semiconductor such as Si can be enlarged by the quantum confinement effects. This was one of the motivations for RE doping of nc-Si, and is often cited as being responsible for suppression of temperature quenching of RE luminescence from nc-Si.

However, some reported results cannot be explained by the band-gap argument alone. It has been reported that in the case of Er-doped nc-Si, a slight separation of Er away from nc-Si is at least as important as the quantum-confinement effect in suppressing the temperature quenching. Thus, in order to further the understanding of high RE luminescence efficiency from RE-doped SRSO, it is important to extend the investigation to include factors other than the increased band gap.

In this letter, we report on the result of such an investigation on Nd-doped SRSO. Nd was chosen because its \( ^{4}F_{3/2} \rightarrow ^{4}F_{9/2} \) and \( ^{4}F_{3/2} \rightarrow ^{4}I_{11/2} \) transitions luminesce at \( \sim 0.9 \) and \( \sim 1.1 \) \( \mu \)m, respectively, which fall within the range of intrinsic nc-Si luminescence. This allows Nd to act as a sensitive probe of the interaction between nc-Si and RE ions. We observe Nd luminescence with only a moderate temperature quenching, and find that the exciton-mediated excitation mechanism applies to Nd in SRSO as well. An analysis of the temperature dependence of Nd luminescence lifetime indicates, however, that an Nd–Si coupling strength that is weak enough to result in a small back-transfer rate but still strong enough to allow efficient excitation through excitons is the key to the efficient Nd luminescence, rather than the increased band gap.

Nd-doped SRSO thin films were deposited by electron-cyclotron-resonance plasma-enhanced chemical vapor deposition.

FIG. 1. Exciton-mediated excitation of RE ions in SRSO. Photogenerated free carriers in nc-Si form excitons that recombine by Auger-exciting the RE ions. Temperature quenching of RE luminescence can occur due to energy back-transfer.

a)Electronic mail: seyoungseo@kaist.ac.kr
sition of SiH₄ and O₂ with concurrent sputtering of Nd. Details of the fabrication procedure can be found in Ref. 3. The Si content was varied from 34 to 50 at. %. Henceforth, the films will be referred to as SiXX films, with XX referring to the Si content in at. %. The Nd content and film thickness, on the other hand, were fixed at ~0.14 at. % and ~1 μm, respectively. Post-deposition rapid thermal anneal under Ar environment at 950 °C for 5 min was used in order to precipitate small Si nanoclusters with large band gaps. 16

Nd³⁺ luminescence even though 488-nm line is not absorbed by Nd³⁺ ions, ensuring that Nd³⁺ luminescence we observe is due to energy transfer from nc-Si. Time-resolved Nd³⁺ PL decay traces were measured at 0.92 μm using an InGaAs:Cs photomultiplier tube and a digitizing oscilloscope.

Figure 2 shows the room-temperature Nd³⁺ PL spectra from Nd-doped SRSO films. Nd³⁺ luminescence peaks at 0.92 and 1.1 μm can clearly be observed. The inset shows the intra-4f transitions responsible for the observed luminescence. The maximum Nd³⁺ luminescence is observed from the Si37 film. The Nd³⁺ PL intensity decreases strongly as the Si content is increased, and becomes nearly undetectable for the Si50 film.

Such dependence of the Nd³⁺ luminescence intensity upon the Si content, and the fact that we observe Nd³⁺ luminescence even though 488-nm line is not absorbed by the Nd³⁺ ions, are consistent with the exciton-mediated excitation mechanism shown in Fig. 1. As at least 1.35 eV is required to excite the transitions observed in Fig. 2, only those nc-Si that are small enough to have excitonic states with energies of 1.35 eV or greater can excite Nd³⁺. Thus, only films with Si content less than 44 at. % show significant Nd³⁺ luminescence, since small excess Si content is needed to precipitate small Si nanoclusters with large band gaps. 16 Similar results were also reported by Franzo et al., who have investigated Nd-implanted SRSO. 3 This excitation model was further supported by excitation spectroscopy, which showed a gradual increase of the Nd PL versus excitation energy (not shown).

Figure 3 shows the temperature dependence of the integrated 0.92-μm Nd³⁺ PL intensity from the Si37 and Si44 films with the background luminescence subtracted. We find that the Nd³⁺ PL intensity decreases by factors of 3 and 7 for the Si37 and Si44 films, respectively, as the temperature is raised from 25 K to room temperature. A similar analysis of the 1.1-μm peak was not attempted due to its overlap with luminescence from the Si substrate at low temperatures, as is shown in the inset. The broad peak centered near 800 nm that appears at low temperatures is ascribed to the intrinsic nc-Si luminescence, as it was observed that hydrogenation results in over fivefold increase of the 800-nm luminescence (not shown).

Figure 4 shows the Nd³⁺ PL lifetime of the Si37 film measured at 0.92 μm. Since the 0.92-μm Nd³⁺ PL peak rides on top of the nc-Si luminescence, the Nd³⁺ PL lifetime was determined as follows. First, the nc-Si PL lifetime was measured at 800 nm, and found to be limited by the system response, which was 10 μs. Such a short nc-Si PL lifetime is attributed to the relatively low annealing temperature used, since temperature in the excess of 1100 °C is usually necessary to obtain optimum nc-Si luminescence. 16 Next, from the PL spectra, the nc-Si contribution to PL at 0.92 μm was estimated. Finally, a double exponential fit to the luminescence decay trace was made with one component fixed to 10-μs lifetime and the estimated nc-Si PL fraction to obtain the Nd³⁺ PL decay trace. We find the Nd³⁺ PL lifetime is quenched much less than the Nd³⁺ PL intensity by tempera-
ture, as it decreases from ~50 to ~40 μs as the temperature is raised from 25 K to room temperature. We note that these values for Nd$^{3+}$ luminescence lifetime are comparable to the values reported from other Nd-doped silica-based thin films.\textsuperscript{17}

Figure 4 indicates that back-transfer is nearly completely suppressed in Nd-doped SRSO, and that the temperature quenching of the Nd$^{3+}$ PL intensity is dominated by activation of other exciton recombination mechanisms that compete with RE excitation. Such suppression of back-transfer, however, cannot be explained by the large band gap of Si nanoclusters. Note that the intrinsic nc-Si luminescence peaks around 800 nm, or 1.55 eV—only 200 meV larger than the energy necessary to excite Nd$^{3+}$ into the $^4F_{3/2}$ level. In the case of Nd-doped bulk GaAs whose band gap is 1.42 eV, the Nd$^{3+}$ luminescence lifetime decreases by more than an order of magnitude as the temperature is raised from 4 to 50 K, and becomes undetectable above 100 K. In fact, temperature quenching of Nd luminescence intensity and lifetime by more than an order of magnitude at 100 K has been reported even in the case of Nd-doped GaP, whose band gap is 2.26 eV.\textsuperscript{18}

In order to investigate other factors that contribute to suppression of back-transfer, the temperature dependence of the Nd$^{3+}$ luminescence lifetime for the Si37 film was analyzed with two models\textsuperscript{9,10} that have been used to describe the back-transfer process. While the physical bases differ slightly, the back-transfer rate in both models can be represented as $W_0 \times f(E_0, T)$, where $W_0$ is the coupling prefactor and $f(E_0, T)$ is a model-specific function of $E_0$ and temperature $T$. As can be seen in Fig. 4, both models fit the experimental data equally well. The values used to fit the data are also similar for both models, and are $\sim 1 - 10 \times 10^5$ s$^{-1}$ and $\sim 100$ meV for $W_0$ and $E_0$, respectively.

The value of $\sim 100$ meV for $E_0$ is in agreement with previously reported values for RE-doped semiconductors with comparable energy mismatches.\textsuperscript{9,10} The value of $1 - 10 \times 10^3$ s$^{-1}$ for $W_0$, on the other hand, is several orders of magnitude smaller than $10^8 - 10^9$ s$^{-1}$ reported for Nd$^{3+}$ doped into GaAs or GaP.\textsuperscript{10} and is the main reason the back-transfer is suppressed. While the values are not very accurate due to large error bars and the possibility of temperature-dependent interaction with other levels of Nd$^{3+}$, the conclusion that the coupling prefactor is very small remains valid. This is shown by the dotted line in Fig. 4, which is the result of a fit using Kik’s model, but with $W_0$ fixed at 1 $\times 10^9$ s$^{-1}$. The fit is less satisfactory, and predicts a steep drop with temperature that is not observed.

The conclusion that the coupling between nc-Si and Nd$^{3+}$ ions is relatively weak is supported by recent reports that the excitation rate of Er$^{3+}$ via nc-Si is $\sim 10^6$ s$^{-1}$,\textsuperscript{19,20} several orders of magnitude smaller than $1 \times 10^9$ s$^{-1}$ reported for Er$^{3+}$ in bulk Si.\textsuperscript{21} As the back-transfer is essentially the reverse of the excitation process except for the presence of the thermal barrier, our value for the coupling prefactor is in good agreement with such results, and indicates that weak coupling between nc-Si and RE ions may be a universal feature of RE-doped SRSO. The importance of such a weak coupling for suppression of back-transfer is also consistent with reports that a slight separation between nc-Si and RE ions strongly suppresses the temperature quenching of RE luminescence in SRSO,\textsuperscript{13-15} as the coupling prefactor will decrease with increasing separation between nc-Si and RE ions. Finally, we note that while our temperature-dependent data suggest that the nc-Si PL lifetime is comparable to the interaction rate between nc-Si and Nd ion in our case, it can be several hundreds of microseconds even at room temperature for high-quality nc-Si.\textsuperscript{16,22} Such a large difference would lead to much greater excitation efficiency, while at the same time further suppressing the back-transfer since the exciton created in the back-transfer process will preferably re-excite the RE ion rather than recombine radiatively. Thus, our results suggest that with judicious control, we can obtain a window of nc-Si and RE ion coupling that would allow for both efficient excitation and suppression of de-excitation.

In conclusion, we have investigated the role of Nd-nanocluster coupling in reducing the back-transfer in Nd-doped SRSO. Nd$^{3+}$ in SRSO are excited via excitons in Si nanoclusters. Small thermal quenching of the Nd$^{3+}$ luminescence was observed and the coupling rate was found to be the order of $1 - 10^5$ s$^{-1}$. This relatively weak coupling leads to small back-transfer and thus small temperature quenching of the luminescence.

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\textsuperscript{1}See, for example, Mater. Res. Soc. Symp. Proc. 422 (1996).