Rare Earth Doping of Silicon-Rich Silicon Oxide for Silicon-Based Optoelectronic Applications

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Rare earth doping of silicon-rich silicon oxide (SRSO) and its application for optoelectronic are investigated. Er, Nd, and Pr doped SRSO thin films were prepared by electron cyclotron resonance enhanced chemical vapor deposition with co-sputtering of target. For the Er-doped SRSO film, we find that by using Si nanoclusters, much of the problems facing Er-doped bulk Si can be solved such that an efficient Er\(^{3+}\) luminescence at room temperature can be obtained with very little temperature quenching. Detailed analysis of time-resolved measurement of the deexcitation process of Er shows, however, that a strong coupling does not lead to carrier-mediated quenching of Er\(^{3+}\) luminescence, as is the case with Er-doped bulk Si. Excitation power dependence of Er\(^{3+}\) luminescence indicates that population inversion of Er may be feasible, in Er-doped SRSO. Luminescence properties of Nd-doped SRSO is similar to Er-doped SRSO, but the temperature dependence of Nd\(^{3+}\) luminescence intensity is different from that of Er\(^{3+}\) luminescence, an effect which we ascribe to its higher transition energy. In contrast, no luminescence could be observed from Pr-doped SRSO. Fabrication and operation of waveguides using Er-doped SRSO thin films were also demonstrated.

I. INTRODUCTION

Rare earth atoms, due to their internal 4f transitions, show sharp luminescence at many important wavelengths. For example, 1.5 µm Er\(^{3+}\) and 1.3 µm Pr\(^{3+}\) luminescence correspond to the minimum loss and minimum dispersion window in silica based optical fiber, respectively. As the 4f electrons of rare earth are well localized and shielded by the outer valence electrons, they display nearly atomic luminescence that is independent of temperature even when doped into other host materials. This property has enabled their use as optical dopants in many photonic applications. Recently, a great interest has risen in using in erbium, as an optical dopant in silicon, in order to develop silicon-based luminescent material for use as a basis in developing silicon-based optoelectronic devices. [2,3]

Recently, as an alternative to bulk silicon, nanoclustered silicon was proposed to overcome the problems of bulk silicon. Due to quantum confinement effect of silicon cluster, nanoclustered silicon have advantages such as wide bandgap and weak carrier-Er\(^{3+}\) interaction displaying very efficient room temperature luminescence. [4–6]

Recently, we have shown that in Er-doped silicon rich silicon oxide (SRSO), which consists of nanocrystalline silicon clusters embedded in an SiO\(_2\) matrix, the internal quantum efficiency of Er\(^{3+}\) can be as high as ~ 10 %. [7] This is close to what has been proposed to be the theoretical maximum to Er\(^{3+}\) luminescence in bulk Si, indicating almost complete suppression of de-excitation mechanisms of Er\(^{3+}\) in SRSO. [3]

In this paper, we report on the photoluminescent properties of rare-earth doped silicon-rich silicon oxide, and demonstrate its optoelectronic application. Er, Nd, and Pr doped SRSO thin films were fabricated. The results of temperature and pump power dependence of Er\(^{3+}\) luminescence indicates that all of possible de-excitations of Er\(^{3+}\) SRSO is strongly suppressed, and high internal quantum efficiency and the possibility of population inversion can be induced, due to these suppression. We also observe Nd\(^{3+}\) luminescence and weak temperature quenching of luminescence from Nd-doped SRSO. As the application of such rare earth doped SRSO thin film, fabrication and operation of strip waveguide will be also given, using Er-doped SRSO.

II. EXPERIMENT
Rare earth doped SRSO thin films with varying silicon-oxygen contents ratio were fabricated by electron cyclotron resonance plasma enhanced vapor deposition with concurrent sputtering of rare-earth target. Detailed fabrication procedure can be found in Ref. [6]. Rutherford backscattering spectroscopy (RBS) analysis showed Si content ($C_{Si}$) of films to range from 33 at.% to 46 at.% In all samples, Er, Nd and Pr content was $\sim 0.1$ at.%, and film thickness was $\sim 1 \mu$m. Post-deposition rapid thermal anneal under Ar environment at 950 $^\circ$C for 5 min was used to crystallize Si nanoclusters. This recipe was shown to result in the optimum Er$^{3+}$ luminescence. [8] 488 nm single line of Ar ion laser was used for optical pumping source. All photoluminescence (PL) spectra were measured using a 1/4 m monochromator and general lock-in technique. We used Si and InGaAs photodiodes to detect PL in visible and infrared range, respectively. All PL spectra were corrected for the system response. Digitizing oscilloscope was also used for measurement of Er$^{3+}$ PL decay traces. Low temperature PL spectra were measured using a closed-cycle He cryostat.

III. ER-DOPED SRSO

Figure 1 shows infrared PL spectra of Er-doped SRSO thin films with $C_{Si}$ of 41 at. % and 35 at. % at room temperature. Clearly, 1.5 $\mu$m PL due to $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of $4f$ electrons of Er$^{3+}$ can be observed. Figure 2 shows the temperature dependence of the Er$^{3+}$ PL lifetimes. The inset shows the temperature dependence of Er$^{3+}$ luminescence intensities, normalized at the value of 25 K. We observed virtually no quenching of both the Er$^{3+}$ luminescence lifetimes and its intensities. This is in contrast to Er doped bulk Si, in where, thermal quenching of both excitation and luminescence efficiencies by several orders of magnitude have been reported as the temperature is raised from cryogenic temperature to the room temperature. [2,3] Thus these results also imply that much of problems faced with Er-doped bulk Si can be solved, by using silicon nanoclusters accomplishing efficient Er$^{3+}$ luminescence at room temperature.

In order to study the interaction between Er ions and excess free carriers in Er-doped SRSO, two-beam experiments were performed. Using a variable beam splitter, the excitation beam was split into two beams, one which illuminated the sample continuously, and the other which was chopped by the mechanical chopper. [7] The background illumination ($P$) dependence of Er$^{3+}$ PL decay times is shown in Figure 3(a). The Er$^{3+}$ PL lifetimes decrease as background illumination increases. However the Er$^{3+}$ PL lifetimes decays as only $\sim 0.33$ power of the background illumination intensity. This is much weaker than that in case of bulk Si, where is was shown to decay as $P^{0.5}$. [2] In erbium doped bulk silicon, this quenching of Er$^{3+}$ luminescence by free carriers was shown to make population inversion of Er$^{3+}$ ions impossible. Thus, this weaker Er-exciton interaction of Er-doped SRSO implies
the possibility of population inversion of Er in Er-doped SRSO. To investigate this possibility, the pump power dependence of Er$^{3+}$ luminescence intensity was measured and fitted using two possible models.

In the first model, we assume no saturation of the excitation rate of Er$^{3+}$ ions and limited number of excitable Er$^{3+}$ ions. This model allows for the de-excitation of Er$^{3+}$ by Auger-excitation of excess free carriers and population inversion, however neglects the de-excitation of trapped carriers by Auger-excitation of excess free carriers. Started from this assumption, rate equation can be written and the number of excited Er$^{3+}$ ions ($N_{Er}^x$) can be immediately deduced at steady state because all rate equation zero. Detailed explanations this modelling is given in Ref. [7]. We may then write

$$N_{Er}^* = \frac{a_{ex}N_{Er}P}{a_{ex}P + W(P)}$$

where $N_{Er}$, $a_{ex}$, $W(P)$, and $P$ are the number of excitable Er$^{3+}$ ions, the excitation coefficient, the pump-power dependent luminescent decay rate (as measured in Figure 3(a)) and the pump power, respectively.

In second model, we assume that Er$^{3+}$ PL intensity is saturated and population inversion is not possible, due to the de-excitation of excited Er$^{3+}$ ions and excitons by Auger-excitation involving excess free carriers. This model was shown to be applicable to Er-doped bulk Si.

We write

$$N_x = \frac{a_xn^2}{W_x + cn}; \quad N_{Er}^x = \frac{W_x}{W(P)} N_x = \frac{c_1P^{26}}{W(P)(c_2 + P^{26})}$$

where $c_1$ and $c_2$ are fitting parameters to be determined and $N_x$ and $W_x$ are the number of excitons and exciton decay rate, respectively. The Er$^{3+}$ PL intensities is proportional to $N_{Er}^*$ and spontaneous radiative decay rate of Er$^{3+}$ ions, thus Er$^{3+}$ PL intensity can be described with $P$.

The data and the results of the fit are shown in Figure 3(b). The symbols, solid lines, dotted lines are experimental data, results of fitting using equation 1 and results of fitting using Equation 2, respectively. Clearly, as Figure 3 Equation (1) fits the power dependence of Er$^{3+}$ PL intensity much better than Equation 2 does, indicating that population inversion of Er$^{3+}$ ions in SRSO is indeed possible. Thus realization of Si-based active optoelectronic components such as lasers and amplifiers may be feasible using Er-doped SRSO.

**IV. OTHER RARE EARTH DOPED SRSO**

Nd-doped SRSO thin films with $C_{Si}$ in range from 34 to 46 at. % with Nd content of ~ 0.1 at.% were produced using the same fabrication process as that of Er doped SRSO. Figure 4 shows Nd$^{3+}$ photoluminescence from Nd doped SRSO detected by InGaAs photodiode at room temperature. We can observe 0.92 $\mu$m and 1.06 $\mu$m Nd$^{3+}$ luminescences by $^4F_{3/2} \rightarrow ^4I_{13/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ 4f transition of Nd$^{3+}$, respectively. The inset of figure 4 shows 0.92 $\mu$m Nd$^{3+}$ PL spectra detected with silicon photodiode. The significance of Nd doping is that the 0.92 $\mu$m Nd$^{3+}$ luminescence due to $^4F_{3/2} \rightarrow ^4I_{11/2}$ 4f transition, which unlike the Er$^{3+}$ luminescence, can be detected with a Si photodiode. These results imply the possibility that both Si-based light emission and light detection capabilities can be integrated into one single device. These Nd$^{3+}$ luminescences can not have been observed from Nd doped bulk silicon, because bandgap of bulk silicon is smaller than these 4f transition energies of Nd$^{3+}$. The wide bandgap of SRSO due to quantum confinement effect of SRSO enables excitation of Nd$^{3+}$.

The Figure 4(a) shows $C_{Si}$ dependence of Nd$^{3+}$ PL intensities. Squares and circles are Nd$^{3+}$ PL intensity at 0.92 $\mu$m and 1.06 $\mu$m, respectively. Maximum PL intensity appeared from sample with $C_{Si}$ of 37 at.%. The effect of $C_{Si}$ for Nd$^{3+}$ PL intensities is similar to that for Er$^{3+}$ PL in SRSO. However, while Er$^{3+}$ PL intensities are only weakly dependent upon the $C_{Si}$ within the range.

![Fig. 4. Nd$^{3+}$ PL spectra from samples with in range from 34 to 46 at. % detected with InGaAs photodiode. The inset shows Nd$^{3+}$ PL by $^4F_{3/2} \rightarrow ^4I_{13/2}$ transition of 4f electrons detected Si-diode.](attachment:image.png)
Fig. 5. (a) Si content dependence of Nd$^{3+}$ PL intensities at 920 nm (square) and 1060 nm (circle): (b) Nd$^{3+}$ PL spectra from Nd-doped SRSO with silicon content of 37 at.%, at 25, 100, 200, and 300 K, respectively.

of 34 and 44 at.%, [8] very weak Nd$^{3+}$ luminescences are observed from Nd-doped samples with $C_{\text{Si}}$ of > 44 at.%. Based on previously published results about size effect on bandgap of Si nanocluster, [10] the largest Si clusters, which can still excite Nd$^{3+}$ ions, may be smaller than ones that can excite Er$^{3+}$. As average size of Si nanoclusters increases with $C_{\text{Si}}$, [9], it follows that the upper limit for $C_{\text{Si}}$ for Nd$^{3+}$ luminescence is smaller than that for Er$^{3+}$ luminescence.

Figure 5(b) shows Nd$^{3+}$ PL spectra from sample with $C_{\text{Si}}$ of 37 at.% at 27 K, 100 K, 200 K and 300 K, respectively. Excitation beam power was 800 mW. In general, Nd$^{3+}$ PL intensity increases as temperature decrease by factor of $\sim 5$. This thermal quenching is smaller than that of bulk Si, but, this is larger than that of Er-doped SRSO. [7], indicating that suppression of back-transfer for Nd$^{3+}$ luminescence is not as complete as it is for Er$^{3+}$ luminescence. For back-transfer, thermal energy is needed to bridge the energy mismatch between the 4$f$-transition energy and the exciton formation energy. For the Nd$^{3+}$, this mismatch is smaller than Er$^{3+}$, because 4$f$ transition energy of Nd$^{3+}$ is larger than that of Er$^{3+}$. Thus, this smaller energy mismatch will induce more remarkable thermal quenching of the rare-earth luminescence, as shown.

However this explain is not clear yet. As shown in Figure 5, 1.06 µm Nd$^{3+}$ PL intensity increases by factor of 6 as temperature decrease from 300 K to 27 K, while 0.92 µm Nd$^{3+}$ PL intensity increases by factor of 4. These behavior can not be explained by the correlation between 4$f$ transition energy and energy mismatch, because 1.06 µm Nd$^{3+}$ transition energy is smaller than 0.92 µm Nd$^{3+}$ transition energy. Moreover, we have failed to observe 1.3 µm luminescence from Pr doped SRSO, in spite of several trials (not shown). Taken together, these results indicate that while energy transition model, which was successfully applicable to Er$^{3+}$, is generally true, the energy transition and interaction between 4$f$ electrons of rare earth ions and trapped excitons differ among the different rare earth atoms and among the different 4$f$ states.

V. APPLICATION

One of the simplest optoelectronic application of these rare earth doped SRSO is planar waveguide using Er-doped SRSO thin film. As an example of such waveguide, a slab-waveguide using a 1.3 µm thick Er-doped SRSO film deposited on Si substrate with a 5 µm thick oxide layer was fabricated. Figure 6 shows a CCD camera image of 1.3 µm light confined in such a waveguide, showing

Fig. 6. 1.3 µm confined light from slab waveguide using Er-doped SRSO films detected CCD camera.

Fig. 7. (a) Top view (upper) and quarter view (lower) of SEM images of erbium-doped SRSO strip waveguides: (b) 1.54 µm Er$^{3+}$ PL spectra from such waveguide. The inset figure shows the schematic setup of the experiment.
good light confinement. [11] And we demonstrate erbium doped SRSO strip waveguides. Prior to fabrication, erbium doped SRSO film, 1.5 µm thickness with C_{Si} of 34.1 at.% and Er content of 0.1 at.%, was deposited on 1 µm thick thermally-grown silicon oxide wafer and annealed at 950 °C for 20 min, for the basis of waveguide. These deposition and annealing condition were followed using the recite for optimum Er^{3+} PL luminescence. [8] The refractive index and the bulk optical loss at 1.55 µm was 1.4817 and 4.0 dB/cm, respectively. By photolithography, line with 5 µm width was shaped on the top surface of the SRSO films. Finally, using the standard plasma etch process for SiO_{2} was used to fabricate the waveguides. No more additional treatment was followed after SiO_{2} etching process.

Figure 7(a) shows top view (upper) and quarter view (lower) of the scanning electron microscope image of fabricated strip waveguide. Note that surface is very smooth without any post treatment. The etching depth was 2.6 µm from surface of SRSO film, thus not only SRSO but also SiO_{2} layer were completely etched away. Figure 7(b) shows Er^{3+} PL spectra measured from an end face of such waveguide when 477nm line of Ar ion laser was normally incident upon the waveguide. (see schematic inset of figure 7(b)) Internal Er^{3+} luminescence are well detected, until the distance from end face of waveguide is up to 3 cm.

VI. CONCLUSION

We investigated luminescent properties of rare-earth doped silicon-rich silicon oxide, and discussed their implication for optoelectronic application. For the Er-doped SRSO, the high internal quantum efficiency and the population inversion can be feasible, due to strong suppression of de-excitation for Er^{3+}. Excitation process of Nd^{3+} is slightly different to the case of Er^{3+} and 1.3 µm Pr^{3+} luminescence could not be observed. Thus different excitation model for different rare-earth ions in SRSO may need to be employed. Finally, we could verify the feasibility of optoelectronic application, by fabricating and operating the strip waveguide based on Er-doped SRSO films.

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