Effect of ion-irradiation induced defects on the nanocluster Si/Er\textsuperscript{3+} coupling in Er-doped silicon-rich silicon oxide

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The effect of ion-irradiation induced defects on the nanocluster Si/Er\textsuperscript{3+} coupling in Er-doped silicon-rich silicon oxide (SRSO) thin film is investigated. Er-doped SRSO, which consists of silicon nanoclusters (nc-Si) in a SiO\textsubscript{2} matrix, was fabricated using electron-cyclotron resonance plasma enhanced chemical vapor deposition using SiH\textsubscript{4} and O\textsubscript{2} with concurrent sputtering of Er followed by a high temperature annealing. Defects were introduced into the film via irradiation with 3 MeV Si ions and subsequently removed by high temperature annealings. The authors find that ion irradiation reduces Er\textsuperscript{3+} luminescence from SRSO films, even when the excitation cross section and luminescence efficiency of Er\textsuperscript{3+} ions are completely restored. On the other hand, ion irradiation decreases the intrinsic nc-Si luminescence and has little effect on the Er\textsuperscript{3+} luminescence from a similarly prepared, Er-doped SiO\textsubscript{2} film, indicating that the presence of irradiation induced defects in the initial amorphous film can reduce the number of Er\textsuperscript{3+} ions available for nc-Si mediated luminescence by as much as a factor of 3.

A great interest lies in obtaining efficient light emission from a silicon-based material for use in both long-distance telecommunications and short-distance, inter- and intrachip optical interconnects. Of the many possible approaches, Er diffusion of atoms in an amorphous film is strongly influenced by the initial amorphous film, yet the film. However, both Si and Er need to diffuse in order for Er to precipitate from the initial amorphous film, and Er occurs in nanometer scale\textsuperscript{12–14} and is therefore critically important wavelength of 1.5 \mu m.\textsuperscript{4,5} However, while sensitization has been universally reported, there remains a great deal of controversy regarding the details of the process. In particular, there has been a great uncertainty regarding the fraction of doped Er that can be excited via nc-Si, as the reported values range from less than 1% (Ref. 6) to 10\textperthousand–20\textperthousand (Refs. 7 and 8) to near 100\textperthousand.\textsuperscript{9} Recently, however, it was shown that the formation of nc-Si and their interaction with Er can lead to reduction of Er\textsuperscript{3+} photoluminescence (PL).\textsuperscript{10,11} The interaction between nc-Si and Er occurs in nanometer scale,\textsuperscript{12–14} and is therefore critically dependent on the detailed microstructure of the final film. However, both Si and Er need to diffuse in order for nc-Si to precipitate from the initial amorphous film, yet the diffusion of atoms in an amorphous film is strongly influenced by defects.\textsuperscript{15,15} Thus, the presence of atomic defects in the initial amorphous film will greatly impact the microstructural evolution of the silicon-rich silicon oxide (SRSO) film microstructure (e.g., Er incorporation in nc-Si or Er clustering), even when they are ultimately removed. This is particularly significant for deposition methods such as sputtering or ion implantation that subject the film to bombardments by energetic ions during initial deposition step.

However, while the role of defects induced by ion irradiation on the optical properties of Si nanocrystals has been extensively studied,\textsuperscript{16} so far there has been little investigation into the role of defects in the initial film on the final Er\textsuperscript{3+} luminescence. In this letter, we report on the effect of 3 MeV Si ion irradiation on the nc-Si mediated Er\textsuperscript{3+} PL intensity from Er-doped SRSO films prepared by electron-cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD). We find that ion irradiation strongly decreases the final Er\textsuperscript{3+} luminescence intensity, even though subsequent high temperature annealing completely removes defects, thereby restoring the Er\textsuperscript{3+} excitation cross section and luminescence efficiency. Comparing the results with a similarly prepared, Er-doped SiO\textsubscript{2} film, we conclude that the primary effect of defect generation is reduction of Er\textsuperscript{3+} ions available for nc-Si excitation, by as much as 70\textperthousand. Two Er-doped SRSO films, one with 34 at. \% Si and the other with 35 at. \% Si, were deposited on Si wafers by ECR-PECVD using SiH\textsubscript{4} and O\textsubscript{2} gases with concurrent sputtering of Er.\textsuperscript{3} The Er content was 0.2–0.3 at. \% and the thickness was 200 nm for both films. After deposition, three different combinations of annealing and implantation were used. The first set, henceforth referred to as An, was prepared by annealing the deposited film without any ion irradiation. The second one, henceforth referred to as IrAn, was irradiated after deposition and then annealed. The last one, henceforth referred to as AnIrAn, was first annealed, then ion irradiated, and then annealed again. In all cases, annealing was done for 30 min at 950 °C in flowing Ar environment, and irradiation was done using 3 MeV Si\textsuperscript{++} ions with a dose of 5 \times 10\textsuperscript{15} ions/cm\textsuperscript{2}. The Si ion energy was chosen to ensure that Si ions completely penetrate the deposited film, thus ensuring the irradiation introduces defects only and does not affect the film composition. The ion dose was chosen to en-
sure that defect generation is sufficient to amorphize any possible preexisting Si nanocrystals in the deposited film. For comparison, a pure SiO2 film doped with Er was also prepared and subjected to the same annealing/irradiation steps. Finally, all films were hydrogenated by annealing at 700 °C for an hour in forming gas to passivate any remaining defects.

Figure 1 shows the integrated Er3+ PL intensities from Er-doped SRSO film, measured at room temperature using 200 mW of the 477 nm line of an Ar laser. The 477 nm line was used to ensure that we are observing PL from only those Er3+ ions that are coupled to nc-Si, as the 477 nm line is not absorbed by Er3+ ions. We find that irradiation always results in decreased Er3+ PL intensity by as much as a factor of 3. We also observe that IrAn films consistently give higher Er3+ PL intensity than AnIrAn films, consistent with previous reports. Note, however, that annealing fully restores the Er3+ luminescence lifetimes, as is shown in the inset, indicating that the annealing has fully restored the luminescence efficiency of the optically active Er3+ ions. Same complete restoration of Er3+ luminescence lifetime was observed from the Si 34 at. % film as well (data not shown). As both 34 at. % Si and 35 at. % Si films give similar results, we will henceforth concentrate on the 35 at. % Si film.

Figure 2 shows the pump-power dependence of the nc-Si mediated Er3+ excitation rate, obtained by measuring the difference in the Er3+ PL rise and decay time as the 477 nm pump beam is turned on and off. Again, we find little difference between An and IrAn films. Note also that the slope is also similar between An and IrAn films, indicating that annealing completely restores the effective excitation cross section for nc-Si mediated excitation of Er3+ as well.

Such complete restoration of the excitation and luminescence efficiencies shows that the annealing procedure used here is sufficient to remove any excess defects created by ion irradiation, and that the strong reduction of the Er3+ PL intensity is not due to remaining defects. Rather, the previous data indicate that the defect generation has affected the microstructural evolution of the original amorphous film during annealing to reduce the number of luminescent Er3+ ions.

Interestingly, ion irradiation increases the intrinsic nc-Si PL near 800 nm nearly threefold, as is shown in Fig. 3. This is the exact opposite of the known quenching of the intrinsic nc-Si PL by Er doping due to transfer of energy from nc-Si to Er3+.2,18 suggesting that irradiation breaks coupling between nc-Si and Er3+ ions. Had ion irradiation optically deactivated Er3+ ions while still retaining nc-Si/Er3+ coupling, the nc-Si PL would not have increased, since the mechanism of energy transfer from nc-Si to Er3+ does not depend on the luminescent properties of the coupled Er3+.12 Similarly, were the increase in the nc-Si PL due to formation of more nc-Si, then there would have been a concomitant increase in the Er3+ PL intensity, as the Er concentration of 0.2–0.3 at. % is higher than the typical nc-Si density of 1018–1019 cm−3. The fact that the overall shape and position of the nc-Si PL peak do not change significantly, as is shown in the inset of Fig. 3, also indicate that ion irradiation does not significantly change the nc-Si size distribution.

Note, however, that since we are using the 477 nm line of the Ar laser, we are only probing those Er3+ ions that coupled with nc-Si. Thus, it is not clear whether Er3+ ions decoupled from nc-Si by ion irradiation are still optically active. Since a SRSO film with 35 at. % Si is more than 95% SiO2 by volume, we have prepared an Er-doped, stoichiometric SiO2 film and subjected it to the same irradiation and annealing procedures. The resulting Er3+ PL spectra, obtained using 300 mW of the 488 nm line of an Ar laser to excite Er3+ ions through direct optical absorption are shown in Fig. 4. We find that annealing of ion-irradiated, Er-doped SiO2 results in near complete recovery of the Er3+ PL intensity. Furthermore, as the inset shows, annealing completely restores the Er luminescence lifetimes for SiO2 as well, in agreement with previous reports.

Taken together, Figs. 1–4 present a consistent picture of reduced nc-Si/Er coupling in ion-irradiated SRSO, even though there still remains a possibility that ion irradiation of Er-doped SRSO, unlike that of pure SiO2, optically deactivates Er3+ ion due to reaction of Er with excess Si. While the...
mechanism for such reduced coupling still needs to be investigated in more detail, it is worthwhile to note that the reported values for the nc-Si/Er interaction distance from sputter-deposited films, which experience energetic ion bombardment during deposition, are consistently shorter (around 0.4 nm)\textsuperscript{13,14} than that reported for ECR-PECVD or thermal oxide matrix (around 2 nm) that do not experience such ion bombardment.\textsuperscript{20,21} From application point of view, however, the implication of the results presented here is clear. Ion irradiation reduces the nc-Si/Er coupling as to render that it is impossible for IrAn and AnIrAn films to provide optical gain via nc-Si mediated excitation, since at most 30% of doped Er ions can be excited even under the best case scenario (e.g., no optical deactivation of any Er\textsuperscript{3+}).

In conclusion, we have investigated the effect of ion-irradiation induced defects on the nanocluster Si/Er\textsuperscript{3+} coupling in Er-doped SRSO thin film. The presence of irradiation induced defects in the initial amorphous film can reduce the nc-Si/Er coupling by as much as a factor of 3, making obtaining optical gain via nc-Si mediated excitation impossible. The results suggest that in order to obtain gain, it would be preferable to avoid energetic ion bombardment during deposition, possibly through in situ formation of nc-Si and Er-doped silica.

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