Composition dependence of room temperature 1.54 \( \mu \text{m} \) Er\(^{3+} \) luminescence from erbium-doped silicon:oxygen thin films deposited by electron cyclotron resonance plasma enhanced chemical vapor deposition

Jung H. Shin,\(^a\) Mun-Jun Kim, Se-young Seo, and Chochoon Lee
Department of Physics, Korea Advanced Institute of Science and Technology (KAIST), Yusung-gu, Taejon, Korea

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The composition dependence of room temperature 1.54 \( \mu \text{m} \) Er\(^{3+} \) photoluminescence of erbium-doped silicon:oxygen thin films produced by electron cyclotron resonance plasma enhanced chemical vapor deposition of Si\(_4\) and O\(_2\) with concurrent sputtering of erbium is investigated. The Si:O ratio was varied from 3:1 to 1:2 and the annealing temperature was varied from 500 to 900 °C. The most intense Er\(^{3+} \) luminescence is observed from the sample with a Si:O ratio of 1:1.2 after a 900 °C anneal and the formation of silicon nanoclusters embedded in the SiO\(_2\) matrix. The high active erbium fraction, efficient excitation via carriers, and high luminescence efficiency due to the high quality SiO\(_2\) matrix are identified as key factors in producing the intense Er\(^{3+} \) luminescence.


Erbium in its trivalent state luminesces at 1.54 \( \mu \text{m} \), corresponding to an intra-4f shell transition from the first excited state \( \left( ^4I_{13/2} \right) \) to the ground state \( \left( ^4I_{15/2} \right) \). As an optical dopant in silicon, it offers the possibility of combining, on the same silicon substrate, the capability to process the optical signal with the excellent data processing performances of silicon-based integrated circuits. Since the initial study,\(^1 \) intense research has resulted in significant progress in erbium doping of silicon.\(^2 \)

Several techniques [e.g., ion implantation,\(^3 \) molecular beam epitaxy (MBE),\(^4,5 \) and metal-organic chemical vapor deposition (MOCVD)\(^6 \)] have been used to dope silicon with erbium. From the practical point of view, direct deposition of high quality erbium doped silicon film is desired. This is especially true for hydrogenated amorphous silicon (a-Si:H), which cannot tolerate the high temperature anneals needed to anneal out the implantation damage. In this letter, we report on a new method to deposit erbium-doped Si:O films using electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD) of Si\(_4\) and O\(_2\) with concurrent sputtering of erbium, and on the 1.54 \( \mu \text{m} \) Er\(^{3+} \) luminescence from such films. We will also discuss the effect of varying the composition and annealing conditions on the luminescence intensity.

The experimental setup is shown schematically in Fig. 1. Argon (99.9999\%) plasma is created in the ECR cavity. Si\(_4\) (99.999\%) and O\(_2\) (99.995\%) gases are introduced downstream via a dispersal ring. We have deposited device-quality a-Si:H films using this system. The key point is that in an ECR plasma the ion density is high while the pressure is low such that a target can be efficiently sputtered by a simple negative DC bias.\(^7 \) Thus, an Er target (2 cm diameter, 99.9\%) is located between the ECR cavity and the dispersal ring, and biased negatively. The sputtered Er atoms are ionized in the plasma, carried downstream, and deposited, thus avoiding the ligand contamination problem associated with MOCVD of Er.\(^8 \)

The system base pressure is 1 \( \times 10^{-7} \) Torr. The substrates used are p-type silicon [100] wafers. The deposition temperature, microwave power, and the erbium target bias were kept constant at 300 °C, 400 W, and \(-200 \) V, respectively, for all samples. The Si\(_4\), O\(_2\), and Ar flow rates were adjusted to give the desired Si\(_4\):O\(_2\) flow ratio while keeping the deposition pressure and erbium target current at 7 \( \times 10^{-5} \) Torr and 40 mA, respectively. After deposition, some samples were rapid thermal annealed at 500, 700, and 900 °C for 7.5 min in flowing Ar atmosphere. Er\(^{3+} \) photoluminescence (PL) was measured at room temperature with an Ar laser at a nominal pump power of 50 mW, a 25 cm monochromator, and a non-cooled Ge detector without employing the lock-in technique. PL excitation spectroscopy was performed using the single lines of an Ar laser in the wavelength range 455–515 nm.

Rutherford backscattering spectroscopy (RBS) showed that the deposited films were \( \approx \) 700 nm thick with a uniform erbium concentration of \( \approx 0.2 \) at. % (not shown). The silicon:oxygen ratio, Q, was found to be 3:1, 1.7:1, 1:1.2, 1:1.9,

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\(^a\)Electronic mail: jhs@sorak.kaist.ac.kr

![FIG. 1. Schematic representation of the ECR-PECVD deposition system.](image-url)
and 1:2 for SiH₄:O₂ flow ratios of 2:1, 1.5:1, 1:1, 1:1.3, and 1:2, respectively. As-deposited samples are also expected to contain ~10 at. % hydrogen. Figure 2 shows the fixed-θ X-ray diffraction (XRD) spectra for samples with Q of 3:1, 1:1.2, and 1:2, both as deposited and after a 900 °C anneal. As-deposited samples are amorphous. The broad peak near 28° from the as-deposited sample with Q of 3:1 is attributed to amorphous Si. After the 900 °C anneal, silicon crystallites form in silicon-rich samples, as evidenced by the Si [111] reflection peaks. From the width of the diffraction peak, we estimate the crystal size to be in the nm range. No silicon crystals form in the sample with Q of 1:2. The small peak at 29.2° is due to Er₂O₃ [222] reflection. We attribute this formation of Er₂O₃ to the presence of excess oxygen ions in the plasma, resulting in reactive sputtering of Er to a small degree. Such presence of excess oxygen ions is not surprising as SiH₄:O₂ flow ratio of 1:1.3 was already sufficient to produce nearly stoichiometric SiO₂ with Q of 1:1.9. Taken together, the RBS and XRD data indicate that the samples range from oxygen-doped hydrogenated amorphous silicon (a-Si:H:O) to SiO₂.

Figure 3 shows the PL spectra, displaying the characteristic Er³⁺ luminescence. The intensities are corrected for the slight sample-to-sample variation in thickness and Er concentration. The large signal-to-noise ratio of the PL spectra without the benefit of cooling or lock-in technique shows how intense the luminescence really is. The Er³⁺ luminescence intensity initially increases with increasing oxygen content, reaching the maximum at Q of 1:1.2, but decreases with a further increase in oxygen content. The inset shows the integrated Er³⁺ PL intensities as functions of the anneal temperature. Note the different scales for each sample. A clear composition dependence of the effect of annealing is observed. Samples with Q of 1:1.9 and 1:2 do not luminesce as deposited, and require high temperature annealing for Er⁵⁺ luminescence. On the other hand, samples with Q of 3:1 and 1.7:1 luminesce most brightly as deposited, and annealing quenches the Er³⁺ luminescence from these samples. The Er³⁺ luminescence intensity from the sample with Q of 1:1.2, too, initially decreases upon annealing, but drastically increases after 900 °C attaining the maximum intensity of all the samples.

In general, we need to (1) increase the active Er fraction; (2) increase the excitation efficiency; and (3) increase the luminescence efficiency (i.e., increase the fraction of excited Er atoms that decay radiatively) in order to increase the total Er³⁺ luminescence intensity. The increase of Er³⁺ luminescence from SiO₂-like films (the samples with Q of 1:1.9 and 1:2) by annealing is attributed to such an increase in luminescence efficiency through the removal of defects in the SiO₂ matrix (e.g., OH bonds) that act as non-radiative recombination sites for excited Er atoms. The quenching of the Er³⁺ luminescence from a-Si:H:O-like films by annealing is attributed to creation of defects by annealing, first by outdiffusion of hydrogen that passivates defects inherent in a-Si:H:O, then by polycrystallization and subsequent formation of grain boundaries. Such defects can act both as recombination sites for carriers, thus lowering the excitation efficiency, and as non-radiative decay paths for excited Er³⁺ atoms, thus lowering the luminescence efficiency. Note that in this case of a-Si:H:O doped with Er deposited by ECR-PECVD the negative impact of annealing always outweighs its possible benefits. This is in contrast to Er implanted a-Si:H:O, where a compromise must be made between the loss of hydrogen and the removal of implantation damage by annealing, and demonstrates the advantage of direct deposition.

The initial increase in Er³⁺ luminescence with an increase in oxygen concentration is attributed to an increase in the active Er fraction, as oxygen is known to activate Er in Si. The decrease in Er³⁺ luminescence with a further increase in the oxygen concentration is attributed to a transition from carrier-mediated excitation to optical excitation of Er. This is confirmed by the excitation wavelength dependence of the Er³⁺ luminescence intensity, as shown in Fig. 4. To clarify the trend, the intensities are normalized to the value at the excitation wavelength of 515 nm. Nearly identical to Er implanted SiO₂ samples with Q of 1:1.9 and 1:2 luminesce only near the excitation wavelengths of 488 and 515 nm, reflecting the 415/2 → 4F⁷/₂ and 415/2 → 2H¹₁/₂ optical absorption bands of Er³⁺, respectively. Samples with higher silicon content display Er³⁺ luminescence for all excitation wavelengths, indicating that the excitation of Er is...
dominated by carrier recombination. The optical absorption cross section of \( {\text{Er}^3^{+}} \) is rather small, of the order of \( 10^{-20} \) cm\(^2\). Thus the overall \( {\text{Er}^3^{+}} \) luminescence intensity from SiO\(_2\) can be lower than that from a-Si:H:O despite the higher active Er fraction and higher luminescence efficiency.

The most intense \( {\text{Er}^3^{+}} \) luminescence is observed from the sample with Q of 1:1.2 after a 900 °C anneal, coinciding with formation of silicon nanoclusters. Such a matrix of SiO\(_2\) with embedded Si nanoclusters is usually referred to as silicon rich silicon oxide (SRSO). Figure 4 shows that the excitation of Er in SRSO is still dominated by carrier recombination, indicating that (1) despite the small volume fraction of Si clusters, the matrix as a whole remains semiconducting; (2) the clusters and the surrounding oxide matrix are of high electrical quality. Indeed, a SRSO with a nearly identical Si:O ratio and thermal treatment as the one presented in this letter was confirmed by transmission electron microscopy to contain high-quality Si nanocrystals. In addition, the Er-doped SRSO was confirmed not to show any luminescence, either visible or infrared, that could be related to defects in SiO\(_2\), suggesting that the oxide matrix surrounding the silicon nanoclusters is also of high quality (not shown).

Thus, we attribute the intense \( {\text{Er}^3^{+}} \) luminescence from SRSO to its having the right balance of Si and O to satisfy all three above-mentioned requirements for intense \( {\text{Er}^3^{+}} \) luminescence. Due to its high oxygen content, it has a high active Er fraction. Yet it contains enough Si clusters of high quality that carrier-mediated excitation, which was shown to be more efficient than direct optical absorption, still dominates. Furthermore, the luminescence efficiency is high due to the high quality oxide matrix. Others have shown that SRSO films produced by oxidation of porous silicon doped electrochemically with erbium show room temperature \( {\text{Er}^3^{+}} \) luminescence. Our results suggest that SRSO, by combining the advantages of SiO\(_2\) and a-Si:H:O, may be a more efficient host material for Er than either one alone. We should note that it is likely that the large band gap of SRSO also contributes to the intense \( {\text{Er}^3^{+}} \) luminescence, as it was shown that a larger band gap of the host matrix tends to reduce the temperature quenching of the luminescence intensity. However, as the temperature quenching of \( {\text{Er}^3^{+}} \) luminescence from a-Si:H:O (Ref. 8) and from SRSO produced by oxidation of porous silicon are about equal, the large band gap of SRSO alone cannot explain its greater \( {\text{Er}^3^{+}} \) luminescence intensity over a-Si:H:O. SRSO can also luminesce in the visible range if carriers can be confined effectively in the Si nanoclusters. However, a sample without erbium did not show any visible luminescence, indicating that in this case the clusters were either too large or too close together for quantum confinement of carriers to be effective.

In conclusion, we have developed a method to directly deposit erbium-doped Si:O films ranging from a-Si:H:O to SiO\(_2\) using ECR-PECVD of SiH\(_4\) and O\(_2\) with concurrent sputtering of erbium, and demonstrated intense room temperature \( {\text{Er}^3^{+}} \) luminescence from such films. The most intense luminescence is observed from SRSO films containing silicon nanoclusters, and is attributed to the favorable combination of high oxygen content and the good semiconducting qualities of the SRSO.

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