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The effect of hydrogenation on the room-temperature 1.54 μm Er^{3+} photoluminescent properties of erbium-doped silicon-rich silicon oxide thin films is investigated. Two samples with 7 and 1 at. % excess silicon and 0.4 at. % erbium were prepared by electron cyclotron resonance plasma-enhanced chemical vapor deposition of SiH$_4$ and O$_2$ with cosputtering of erbium and subsequent rapid thermal anneal at 900 °C. Hydrogenation by exposure to D plasma doubles the 1.54 μm Er^{3+} luminescence intensity from the high excess silicon content sample but halves that from the low excess silicon content sample. The lifetimes and excitation power dependence of Er$^+$ luminescence show that hydrogenation primarily affects the active erbium fraction, increasing it in case of the high excess silicon sample but decreasing it in case of the low excess silicon content sample. With proper treatments, Er^{3+} luminescence lifetime of over 7 ms is obtained. © *1998 American Institute of Physics.* [S0003-6951(98)04351-4]

Silicon is the dominant semiconductor material, but is hardly represented in the field of optoelectronics due to its inability to efficiently emit light. Doping silicon with erbium can result in light emission at 1.54 μm due to the $^4I_{13/2}$ to $^4I_{15/2}$ intra-4f shell transition of Er^{3+}, and thus represents a possible way of truly integrating the signal and data processing capabilities in one single device.[1] Among many silicon-based materials, silicon-rich silicon oxide (SRSO), which consists of nanocrystalline silicon clusters embedded in SiO$_2$ matrix, is unique in that it has all the factors (high oxygen concentration, wide band gap, and low defect density) which are known to enhance the room temperature Er^{3+} luminescence intensity.[2–4] Furthermore, Er^{3+} in SRSO is excited via auger excitation of Er^{3+} 4f shells by electron-hole pair recombination in the silicon nanoclusters,[5,6] thus enabling active electro-optical devices such as light-emitting diodes (LEDs) to be fabricated using Er-doped SRSO.[7] An added benefit is that SRSO can luminesce in the visible range due to recombination of carriers in the clusters,[6,8,9] thus allowing itself to be probed by simple optical means.

In the case of Er^{3+}-doped SRSO as well as all other Er-doped semiconductors, defects play an important role in determining the overall Er^{3+} luminescence. Defects can act as recombination sites for carriers, thus reducing the excitation efficiency of Er^{3+} atoms, or act as nonradiative decay channels for excited Er^{3+} atoms, thus reducing the Er^{3+} luminescence efficiency. Hydrogenation is an effective way of passivating such defects without incurring undue changes in the material itself. Indeed, hydrogenation was shown to be effective in passivating defected silicon nanoclusters in SRSO,[8] and also to enhance erbium luminescence intensity from Er-doped AlN.[10] In this letter, we report on the effect of hydrogenation on the Er^{3+} luminescence properties of Er-doped SRSO. We find that hydrogenation can be either beneficial or detrimental for Er^{3+} luminescence, depending on the excess silicon content of SRSO.

670 nm thick Er-doped SRSO film with 7 and 1 at. %

excess Si and 0.4 at. % of Er were prepared on Si substrates by electron cyclotron resonance (ECR) plasma-enhanced chemical vapor deposition of SiH$_4$ and O$_2$ with cosputtering of erbium and subsequent rapid thermal anneal at 900 °C. The details of the preparation are given in Ref. 2. Er^{3+} photoluminescence (PL) spectra were measured using the 515 nm line of Ar laser, a grating monochromator, a thermoelectrically cooled InGaAs detector, and the standard lock-in technique. Luminescent lifetimes were measured using a digitizing oscilloscope. Laser power was varied from 5 to 800 mW. Visible luminescence was measured using 325 nm line of HeCd laser with GaAs photomultiplier tube, again using lock-in technique, at a pump power of 13 mW. All luminescence measurements were taken at room temperature. Hydrogenation was performed by exposure to deuterium ECR plasma for 30 min at a microwave power of 600 W. The sample was not intentionally heated during hydrogenation, but the plasma heating increased the sample temperature to ~200 °C. Elastic recoil detection of 2 MeV He and secondary ion mass spectroscopy confirmed that about 0.2 at. % of D was incorporated into SRSO films. D concentration was uniform in case of 1 at. % excess Si sample, but decreased with increasing depth in case of the 7 at. % excess Si sample (not shown).

Figure 1 shows the visible PL spectra. No data were taken in the 625–675 nm region in order to avoid the second order diffraction peak of the laser light. As deposited, both 7 and 1 at. % excess Si samples show broad luminescence peaks centered at 780 and 710 nm, respectively, that is typical of SRSO. The blueshift of the luminescence peak with decreasing Si content is consistent with observations by other investigators,[8,11] and is ascribed to the lower excess silicon content sample having smaller sized Si clusters. Upon hydrogenation, the luminescence intensities of 7 and 1 at. % excess Si samples are increased by a factor of about 10 and 30, respectively, indicating that the observed visible luminescence peaks are indeed due to Si nanoclusters and not due to
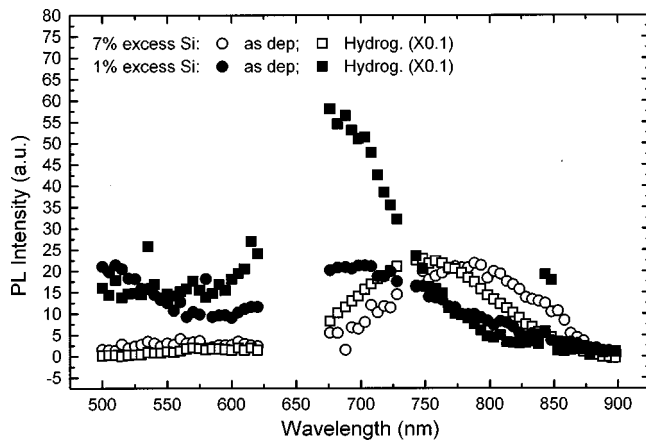
FIG. 1. Room-temperature visible PL spectra showing broad luminescence peak due to Si nanoclusters. No data were taken in the 625–675 nm range in order to avoid the second order reflection of the laser line. Note the different scales for spectra before and after hydrogenation.

FIG. 3. Decay traces and luminescence lifetimes of Er^{3+} PL intensity at room temperature following excitation to steady-state values with pump power of 200 mW. There are two decay traces for the 1 at. % excess sample; they are nearly identical and thus hard to distinguish.

defects in SiO_2, and that defected Si nanoclusters were successfully passivated by hydrogenation.[8] From compilation of positions of PL peaks with cluster sizes,[12] we estimate the Si clusters to be about 3 and 2 nm in diameter for 7 and 1 at. % excess Si samples, respectively. The difference in the amount of luminescence intensity increase seems to indicate that smaller clusters are more affected by hydrogenation than the larger clusters. This is consistent with, and may explain the 30 nm blueshift of luminescence peaks upon hydrogenation that is observed from both samples.

Figure 2 shows infrared PL spectra, displaying the typical 1.54 μm Er^{3+} luminescence. Upon hydrogenation, the Er^{3+} luminescence intensity is about doubled in case of the 7 at. % excess Si content sample, but is about halved in case of the 1 at. % excess Si sample. The exact amount of change upon hydrogenation as well as the relative intensities between different samples depend on the laser power. This is described in more detail later in Fig. 4. It should be noted that in all cases presented in this paper, direct optical excitation of Er^{3+} may be neglected in comparison to carrier-mediated excitation. This was confirmed by photoluminescence excitation spectroscopy (not shown) and by observing that a similarly prepared Er-doped SiO_2 has erbium lumines-
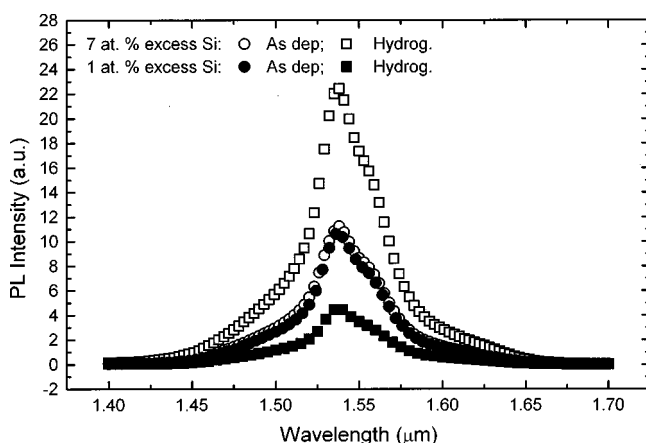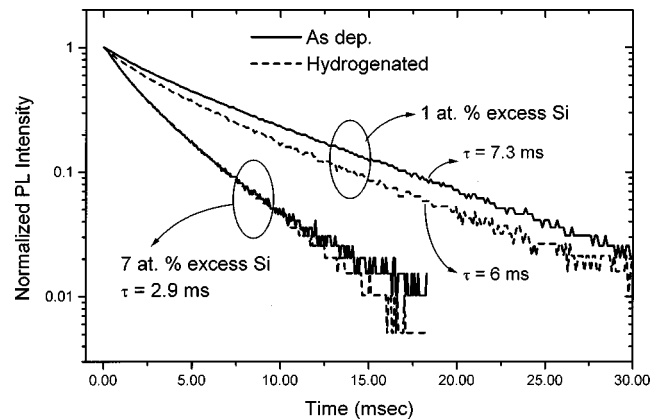
cence intensity that is weaker by a factor greater than 50 for all laser power used.

Figure 3 shows the decay trace of Er^{3+} PL intensity of upon termination of excitation. Before hydrogenation, the decay trace of 7 at. % excess Si sample is nonexponential with an effective luminescent lifetime of 2.9 ms, while that of 1 at. % excess Si sample is nearly single exponential with a luminescent lifetime of 7.3 ms. It should be noted that this is an extremely long Er^{3+} luminescence lifetime, much longer than that reported for any Er-doped semiconductors including wide-band-gap materials such as GaN,[13] and in the same range as that reported for Er-doped glasses.[14] Upon hydrogenation, the decay trace of 7 at. % excess Si sample undergoes absolutely no change. However, that of 1 at. % excess Si sample becomes more non-exponential with a shorter effective lifetime of 6 ms.

The dynamics of Er^{3+} luminescence may be approximated as

$$\frac{dN^*}{dt} = \alpha P(N_o - N^*) - W_{tot}N^*, \qquad (1)$$

where N^* is the number of excited Er^{3+} atoms, P is the excitation power, α is the excitation efficiency, N_o is the total number of optically active Er^{3+} atoms (those capable of luminescing), and W_{tot} is the decay rate of excited Er^{3+} atoms. During the steady state, $dN^*/dt=0$, and

$$I = W_{rad}N^* = W_{rad}\frac{1}{1 + W_{tot}/\alpha P}N_o, \qquad (2)$$

where I is the luminescence intensity and W_{rad} is the radiative decay rate of excited Er^{3+} atoms, taken to be intrinsic to the given material and independent of extrinsic factors such as defect concentration.[14] To obtain information on effect of hydrogenation on α and N_o, the excitation power dependence of Er^{3+} PL intensity was measured and fitted to Eq. (2), as shown in Fig. 4. In all cases, a good agreement is observed. The values of α and N_o, normalized to that prior to hydrogenation, are 1.1 and 1.7 for 7 at. % excess Si sample, respectively, and 1.6 and 0.4 for 1 at. % excess Si sample, respectively.

Figures 3 and 4 show that in case of 7 at. % excess Si sample, hydrogenation and consequent passivation of de-
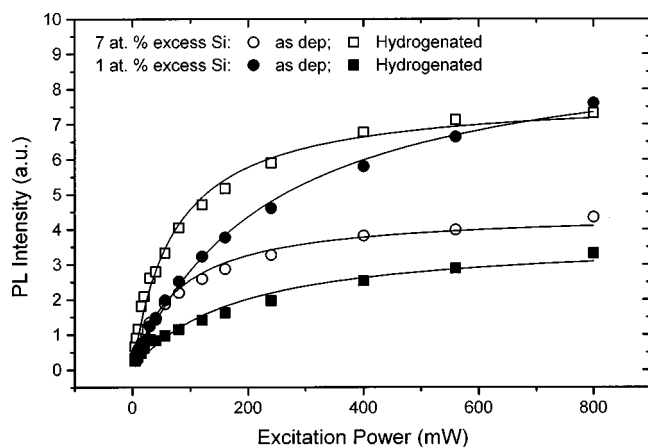

FIG. 2. Room-temperature PL spectra showing the distinct Er^{3+} luminescence.

FIG. 4. Power dependence of Er^{3+} peak PL intensities. The symbols are data points; the curves are results of fit using Eq. (2). The values of α and N_o, normalized to that prior to hydrogenation, are 1.1 and 1.7 for high excess silicon sample, respectively, and 1.6 and 0.4 for low excess silicon sample, respectively.

fected clusters increase the Er^{3+} luminescence intensity by predominantly increasing the active erbium concentration without greatly affecting either the excitation efficiency or lifetime of the Er^{3+} luminescence, suggesting that optically active Er^{3+} atoms are isolated from such defected clusters. As optical activation of previously inactive nanoclusters were shown to be the predominant reason for hydrogenation-induced increase in the cluster luminescence intensity from SRSO, the results presented here indicate that Er^{3+} luminescence in SRSO is dominated by atoms associated with defect-free nanoclusters.

In case of low excess Si content sample, hydrogenation predominantly decreases the active Er^{3+} fraction and, to a smaller degree, the Er^{3+} luminescence lifetime as well even though it passivates defected clusters. It is not clear why such de-activation of Er^{3+} occurs. A possible candidate for such deactivation mechanism is formation of free O–D bonds, which are known to be one of the most important quenching centers in Er-doped glasses.[15] However, infrared absorption measurements did not conclusively show formation of such bonds. Others have shown that hydrogen plasma treatment of Er-doped porous Si is less effective than oxidation in obtaining strong Er^{3+} luminescence,[16] and similar effect may be in operation in this case as well. However, the fact that such de-activation is not observed in case of the 7 at. % sample, which underwent identical treatments, shows the excess Si content must play a role in determining the effect of hydrogenation. We are currently investigating the Er^{3+} excitation and de-excitation mechanisms for possible differences.

In conclusion, we have investigated the effect of hydrogenation on Er^{3+} luminescence from Er-doped SRSO. We find that hydrogenation can increase the Er^{3+} luminescence intensity by increasing optically active Er^{3+} fraction by passivating defected Si nanoclusters, but can reduce the Er^{3+} luminescence intensity by deactivating Er^{3+} atoms if excess Si content is too low.

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