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Photoluminescence excitation spectroscopy of erbium-doped silicon-rich silicon oxide

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The 1.54 μm Er^{3+} photoluminescence excitation (PLE) and photoluminescence (PL) spectra of erbium-doped silicon-rich silicon oxide (SRSO) are investigated. Between 350 and 820 nm, PLE spectra are broad and featureless, and the PL spectra are independent of the excitation wavelengths. The results indicate that in erbium-doped SRSO, the Er^{3+} luminescence is dominated by a single class of Er sites with a strong coupling to all the carriers in the silicon nanograins. © *2000 American Institute of Physics.* [S0003-6951(00)03313-1]

Erbium doping of semiconductors has received much attention recently due to its possibility of developing novel optoelectronic materials.[1] By now, it is widely accepted on the basis of many experimental and theoretical results[2–4] that for an efficient Er^{3+} luminescence at room temperature, wide-band gap materials such as GaN[5] are necessary. However, the band gap of narrow-band gap materials such as Si can be greatly increased by using Si nanostructures instead of bulk Si, taking advantage of the quantum confinement effect.[6] Since such Si nanostructures preserve compatibility with the Si technology, many researchers have investigated the properties of erbium-doped Si nanostructures such as porous Si[7–9] and silicon-rich silicon oxide (SRSO), which consists of Si nanoclusters embedded in a SiO_2 matrix.[10–13] Importantly, it is now well established that in such erbium-doped Si nanocrystals, erbium atoms can be excited efficiently by transfer of energy from Si nanocrystals.[8,10–12] Thus, light emitting diodes using erbium-doped SRSO are possible[13] and the internal quantum efficiency of Er^{3+} luminescence from erbium-doped SRSO can be as high as 18% at room temperature.[14]

However, for devices based on erbium-doped SRSO to be practical, a large fraction of Er^{3+} ions must be accessible to electronic carriers for excitation. In erbium implanted GaN, for example, it was shown that many different erbium sites with distinct excitation mechanisms exist; furthermore, the vast majority of these optically active erbium atoms were found not to be coupled to the carriers, but could be excited by resonant optical absorption only.[15] SRSO is a heterogeneous mixture of Si nanoclusters and SiO_2, with many distinct sites possible. Thus, the site of erbium atoms is an important issue that needs to be clarified for both a better understanding of Er^{3+} luminescence and the eventual development of devices.

In this letter, we report on the results of photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy of erbium-doped SRSO. We find that from 6 K all the way to room temperature, the Er^{3+} luminescence from erbium-doped SRSO is dominated by a single class of site that is accessible for exciation by carriers in all electronic states of SRSO. We identify the interface of Si nanograins and SiO_2 as the possible site of the optically active Er^{3+} ions. It should be noted that throughout this letter, we use the term ''site'' very generally to indicate the overall environment of erbium atoms. It is not intended to indicate a specific lattice site or a particular atomic configuration.

Er-doped SRSO films with Si contents of 35 and 41 at. % with Er content of 0.4 at. % were prepared on Si [100] wafers by electron cyclotron resonance plasma-enhanced chemical vapor deposition (ECR-PECVD) of SiH_4 and O_2 with concurrent sputtering of Er. The thickness of the films was 670 nm. Since as-deposited films are amorphous, films were subsequently rapid thermal annealed at 900 °C for 7.5 min to form Si nanocrystals. We note that the anneal temperature of 900 °C is slightly lower than is customary for precipitation of Si nanocrystals. However, other researchers have directly observed Si nanocrystals of 2-3 nm in diameter in a similarly prepared SRSO film using transmission electron microscopy,[16] and we have previously confirmed the presence of such Si nanocrystals in a comparable erbium-doped SRSO film using x-ray diffraction and PL.[12,17] Zhao *et al.* have reported that erbium doped into amorphous Si can act as nucleation centers and result in Si nanocrystal formation after an anneal of only 10 s at 700 °C,[18] and a similar effect may be operating here. Er^{3+} PL measurements were made using either a HeCd laser, an Ar laser, or a Ti:sapphire laser as the excitation source, and using either a liquid nitrogen cooled Ge detector or a thermo-electrically cooled InGaAs detector and employing the standard lock-in technique. PLE measurements were made using a Xe lamp dispersed by a monochromator. The resolution of the dispersed light was

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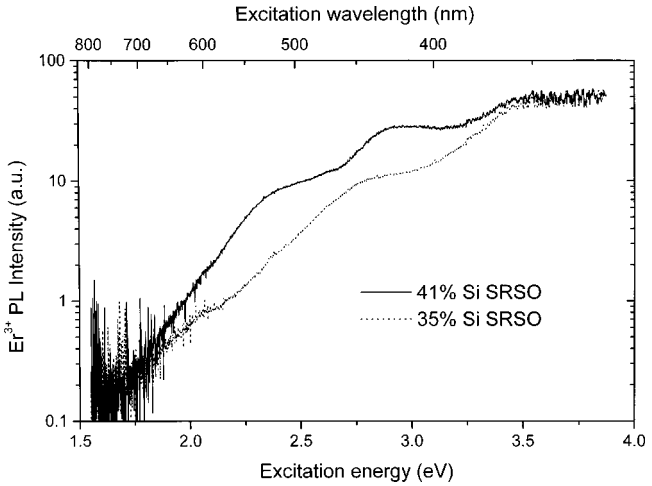

FIG. 1. Photoluminescence excitation spectra of Er^{3+} PL intensity, measured at 1534.5 nm. The temperature during the measurement was 6 K.

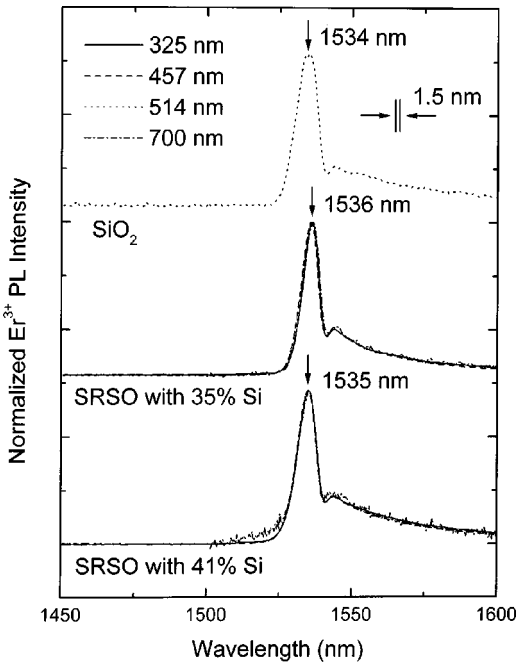

FIG. 2. The normalized Er^{3+} PL spectra of erbium-doped SRSO films measured with pump beam wavelengths of 325, 457, 515, and 700 nm at 6 K. There are four spectra for each of the SRSO films. They are nearly identical and thus hard to distinguish. Also shown for comparison is the Er^{3+} PL spectrum of erbium-doped SiO_2 film, measured with a 515 nm pump beam.

17 nm. The PLE spectra were corrected for the system response.

Figure 1 shows the PLE spectra of the erbium-doped SRSO films measured at 6 K. For the SRSO film with 41 at. % Si, a broad plateau at 425 nm and a knee near 520 nm followed by an exponential tail are observed, while for the film with 35 at. % Si, a plateau at 450 nm is followed by an exponential tail. Other than these, the PLE spectra are smooth and featureless. Specifically, we do not detect any peaks due to direct, resonant optical excitation of Er^{3+} 4f electrons, even though several transitions such as $^4I_{15/2} \rightarrow {}^4F_{15/2}$, $^4I_{15/2} \rightarrow {}^2H_{11/2}$, and $^4I_{15/2} \rightarrow {}^4F_{9/2}$ are expected near the excitation wavelengths of 490, 520, and 650 nm, respectively. The sharp peaks near the beginning and the end of the PLE spectra are system artifacts. No peaks of any kind could be detected even when a Ti:sapphire laser with 50 mW of power was used instead of the Xe lamp to probe the 700–820 nm region for the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ transition (not shown).

Such absence of peaks in the PLE spectra due to the resonant optical absorption of Er^{3+} indicates that in erbium-doped SRSO, the Er^{3+} luminescence is completely dominated by erbium atoms located in sites that are strongly coupled to the carriers in the Si nanocrystals. Indeed, overall the PLE spectra are very similar to the optical absorption spectra of nanocrystalline Si.[19] In such a case, incident light with different wavelengths will generate, in general, different kinds of carriers. The band gap of nanocrystals in the size range of 2 nm is in excess of 2 eV.[20] Thus, a 700 nm pump beam would predominantly create localized carriers, consistent with the long exponential Urbach tail observed in Fig. 1, while a 325 nm pump beam would predominantly create free carriers in the conduction band of Si nanocrystals.

However, varying the wavelength of the pump beam, and thus the nature of the generated carriers, has no effect upon the resulting Er^{3+} PL spectra. This is shown in Fig. 2 which shows the Er^{3+} PL spectra of the erbium-doped SRSO films, measured at 6 K using either 325, 457, 514, or 700 nm light for excitation. The excitation sources used for 325, 457, 514, and 700 nm light were a HeCd laser, an Ar laser, an Ar laser, and a Ti:sapphire laser, respectively, and the excitation powers were 2, 15, 15, and 50 mW, respectively. Also shown for comparison is the Er^{3+} PL spectrum of an erbium-doped SiO_2 film, measured with 515 nm line of Ar laser at an excitation power of 15 mW. The positions of main peaks and the spectral resolution are also indicated. We find virtually no difference between Er^{3+} PL spectra obtained using different excitation wavelengths. Indeed, it is very difficult to tell that there are actually nine spectra in Fig. 2. All Er^{3+} PL spectra from SRSO film with Si content of 41 at. % have a main peak at 1535 nm with full width at half maximum (FWHM) of 8.3 nm followed by a secondary peak at 1544 nm. The Er^{3+} spectrum obtained using 700 nm excitation light does have a slightly different shape, but the peak position is still the same. Similarly, all Er^{3+} PL spectra from SRSO film with Si content of 35 at. % have a main peak at 1536 nm with FWHM of 7 nm followed by a secondary peak at 1544 nm. A very slight variation between spectra can be observed, but the variations are well within the spectral resolution of the PL setup, and in any case are much smaller than the FWHM of the main peak. The Er^{3+} spectrum of erbium-doped SiO_2 film has a main peak at 1534 nm with FWHM of 9 nm followed by a secondary peak at 1544 nm.

Such relatively broad Er^{3+} PL peaks indicate that there is a wide range of possible atomic configurations for erbium atoms in SRSO. To put it another way, the overall environment of erbium atoms is highly disordered. However, the lack of any peaks in PLE spectra and the independence of Er^{3+} PL spectra of the wavelength of the pump beam indicate that in erbium-doped SRSO, these different atomic configurations belong to a single class of erbium sites for Er^{3+} luminescence, and that these sites can be excited by all carriers in the Si nanocrystals irrespective of their electronic state. Such existence of a single class of site is further confirmed by the temperature dependence of the Er^{3+} PL spectra, as shown in Fig. 3. We find that raising the temperature from 12 K to room temperature broadens the PL spectrum

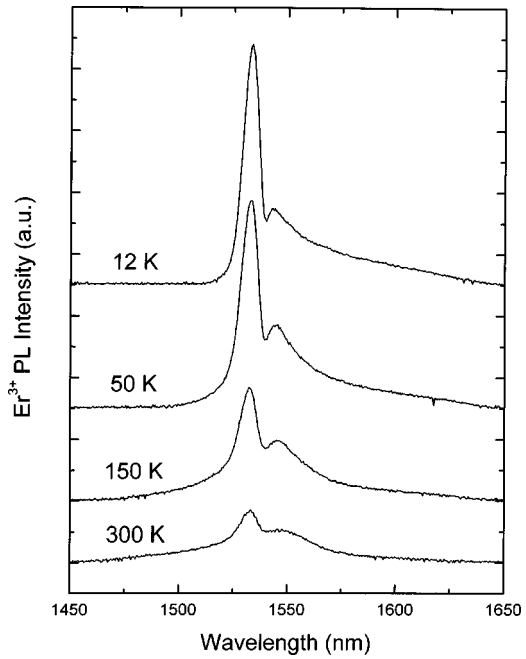

FIG. 3. The Er^{3+} PL spectra of erbium-doped SRSO film with Si content of 35 at. %, measured at different temperatures with a 515 nm pump beam. The curves are offset for clarity.

but does not change the overall shape or the position of the peak. This indicates that the Er^{3+} PL intensity from erbium atoms in different atomic configurations all have the same temperature dependence, making it very likely that they indeed belong to the same class of sites.

The above results and conclusions contrast with those from erbium-doped porous Si, in which two classes of erbium sites, one in Si nanocrystals and the other in the SiO_2 shell, have been identified.[7,9] These two classes of sites were shown to have not only different PL and PLE spectra, with erbium atoms in Si nanocrystals displaying sharp, near-atomic Er^{3+} PL and PLE spectra, but also different temperature dependence of the Er^{3+} PL intensity. We attribute such differences between erbium-doped SRSO and erbium-doped porous Si to the difference in preparation method. In case of erbium-doped porous Si, Si nanocrystals are formed first, followed by erbium doping and subsequent oxidation to form the oxide shell. In the case of erbium-doped SRSO, on the other hand, forming Si nanocrystals by precipitation from a homogeneous SiO_x film is the last step in sample preparation.

As to the actual location of these sites, it is unlikely to be the SiO_2 matrix itself because, as Fig. 2 shows, the Er^{3+} PL spectra of erbium-doped SRSO are different from that of erbium-doped SiO_2. However, the complete absence of sharp peaks in either PL or PLE spectra indicate that erbium atoms are not in a highly ordered, crystalline environment either. Furthermore, the positions of Er^{3+} PL peak from erbium-doped SRSO are 1535 and 1536 nm, which are substantially different from the value found by Stepikhova *et al.*[7] and Dejima *et al.*[9] for Er^{3+} PL from erbium atoms located inside Si nanocrystals. However, erbium atoms must be close enough to Si nanocrystals such that carrier-mediated excitation can be efficient. Therefore, we identify the interface between the Si nanocrystals and SiO_2 matrix as the possible site for the optically active erbium atoms in erbium-doped SRSO. Such conclusion is also consistent with the previous observation that the erbium atoms are in a highly disordered environment.

In conclusion, we have investigated the PL and PLE spectra of erbium-doped SRSO. We find that in erbium-doped SRSO, Er^{3+} luminescence is dominated by erbium atoms in a single class of sites. We identify the interface of Si nanograins and SiO_2 as the possible site of the optically active Er^{3+} ions.

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