

Optical activation of Si nanowires using Er-doped, sol-gel derived silica

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(Received 14 June 2004; accepted 13 December 2004; published online 24 January 2005)

Optical activation of Si nanowires (Si-NWs) using sol-gel derived Er-doped silica is investigated. Si-NWs of about 100 nm diameter were grown on Si substrates by the vapor-liquid-solid method using Au catalysts and H₂ diluted SiCl₄. Afterwards, Er-doped silica sol-gel solution was spin-coated, and annealed at 950 °C in flowing N₂/O₂ environment. Such Er-doped silica/Si-NWs nanocomposite is found to combine the advantages of crystalline Si and silica to simultaneously achieve both high carrier-mediated excitation efficiency and high Er³⁺ luminescence efficiency while at the same time providing high areal density of Er³⁺ and easy current injection, indicating the possibility of developing sol-gel activated Si-NWs as a material platform for Si-based photonics.

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A great interest lies in developing an efficient Si-based light-emitting material that could enable integration of photonics with Si technology.¹ In particular, Er-doping of Si has attracted great attention as it can allow realization of Si-based light emitter in the technologically important 1.5 μm range.² An important advantage of Er-doped Si is that excitation of Er³⁺ is dominated by an Auger-type interaction with carriers, thereby enabling electrical pumping of Er³⁺.

After the initial report,² room-temperature operation of 1.5 μm light-emitting diodes (LEDs) were demonstrated.^{3,4} However, even though the electrical properties of such Si:Er LEDs were excellent, the luminescence efficiencies were quite poor.⁵

Excellent optical properties were obtained by using silicon-rich silicon oxide (SRSO), which consists of nanocluster Si (nc-Si) embedded inside an SiO₂ matrix.⁶⁻⁸ By now, optical gain⁹ as well as efficient light-emitting diodes¹⁰ have been demonstrated using Er-doped SRSO. However, isolation of nc-Si inside the SiO₂ matrix makes current injection into SRSO difficult. Thus, SRSO-based LEDs generally require either very high voltages¹⁰ or very thin SRSO layers that can limit the light output.¹¹ Furthermore, excitation occurs via impact excitation by energetic carriers, which raises questions about the long-term reliability of such devices.

Such problems may be solved by using Si nanowires (Si-NWs) instead. Grown by vapor-liquid-solid (VLS) growth mechanism using metal catalysts, Si-NWs with diameters in the range of 10–100 nm and with length exceeding 1 μm can be grown easily.^{12,13} Furthermore, active electronic devices based on Si-NWs with operating voltages of less

than 5 V have been reported, demonstrating the ease of injection into, and transport along, the Si-NWs.¹⁴

However, previous reports on Er-doping of Si-NWs indicated that Er-doped Si-NWs consisted of Si core with Er-rich, defective polycrystalline surface layer with weak or no Er³⁺ luminescence.¹⁵ On the other hand, there have been reports that the optimum location for Er³⁺ is not inside Si, but in the nanometer-thin oxide shell right next to Si.¹⁶⁻¹⁸ This suggests that rather than trying to dope Si-NWs directly, it would be preferable to coat the Si-NWs with high-quality, Er-doped silica in order to optically activate the Si-NWs.

In this letter, we report on the results of such optical activation of Si-NWs using sol-gel derived Er-doped silica. We observe strong room temperature 1.54 μm luminescence by the Er³⁺ ions in sol-gel derived silica excited via carriers in nearby Si-NWs, with a luminescence lifetime of 6.9 ns and a nearly complete suppression of the temperature quenching. This indicates that by using Er-doped, sol-gel derived silica and Si-NWs, we can create a nanocomposite material that combines the advantages of crystalline Si and Er-doped silica to simultaneously achieve both high carrier-mediated excitation efficiency and high Er³⁺ luminescence efficiency while providing high areal density of Er³⁺ and the ease of carrier injection.

Si-NWs were grown on Si (100) wafers by VLS mechanism in a quartz tube furnace using 2-nm-thick sputtered Au film as the catalyst. During growth, H₂ and Ar gases were introduced at a flow rate of 100 sccm, respectively. SiCl₄ was introduced using H₂ carrier gas that was bubbled through liquid SiCl₄ held at 0 °C at a flow rate of 5 sccm. The growth temperature was 800–900 °C. Er-doped silica sol-gel solution was prepared by first hydrolyzing tetraethylorthosilicate (TEOS) in a 0.05 M HCl aqueous solution with ethanol as the cosolvent. Er-doping was achieved with ErCl₃·6H₂O

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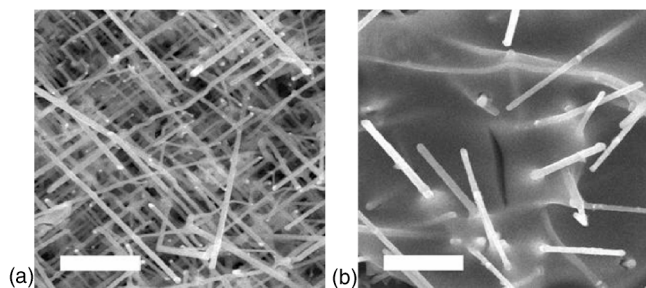


FIG. 1. SEM images of (a) as-grown Si-NWs and (b) Er-doped, sol-gel-derived silica film coated on Si-NWs. Note that the sol-gel solution has completely penetrated the Si-NWs, and that portions of Si-NWs protrude above the silica film, providing direct electrical contacts to the underlying Si substrate. Scale bar represents 2 μm .

with a $\text{ErCl}_3 \cdot 6\text{H}_2\text{O} / \text{TEOS}$ mol ratio of ≈ 1.0 at. %, corresponding to an Er concentration of 0.33 at. % in the finished film. The mixture was then stirred at room temperature for 1 day. The solution was spin coated on the Si-NW grown Si wafers at 1000 rpm for 30 s, and annealed at 450 $^\circ\text{C}$ for 7 h in a flowing N_2/O_2 environment to remove volatile organic compounds. Finally, a rapid thermal anneal at 950 $^\circ\text{C}$ for 5 min in a flowing N_2/O_2 environment was used to activate erbium. The silica layer thickness was about 5 μm . For a comparison, sol-gel derived Er-doped pure silica film without Si-NWs was also deposited on a blank Si wafer using identical procedures. However, the silica layer thickness was only about 0.6 μm in this case. The Er^{3+} photoluminescence (PL) spectra were measured using an Ar laser, a grating monochromator, a thermo-electrically cooled InGaAs detector, and the standard lock-in technique.

Figure 1(a) shows a scanning-electron microscope (SEM) image of as-grown Si-NWs. We observe a dense array of straight Si-NWs of about 100 nm in diameter and 10 μm in length. The Si-NWs lie at an angle of about 60° from the surface normal. Figure 1(b) shows a SEM image of sol-gel derived Er-doped silica film coated Si-NWs. We find that the sol-gel solution has completely penetrated the Si-NW arrays, forming a composite material of Er-doped silica interspersed with Si-NWs. Some macroscopic cracks due to shrinkage of the sol-gel derived film during drying and annealing¹⁹ can also be observed. The volume density of Si-NWs is estimated to be quite low, only about 2.8%. However, due to the high aspect ratio of the Si-NWs and the fact that they lie at an angle, they provide about 11 times more surface area than the substrate alone.

Figure 2 shows the room temperature PL spectra of the Si-NWs and the pure Er-doped silica thin film, pumped with the 473 nm line of an Ar laser. The 473 nm line was chosen because it is absorbed only by Si-NWs and not directly by Er^{3+} ions. This ensures that Er^{3+} excitation occurs via carriers only, and represents an accurate simulation of the situation under current injection. The intensities are scaled by the film thickness to facilitate direct comparisons. We observe strong Er^{3+} luminescence at 1.54 μm from the Si-NWs, indicating energy transfer from carriers in Si-NWs to Er^{3+} ions. On the other hand, we observe hardly any luminescence from the pure silica film. However, the pure silica film does show Er^{3+} luminescence when Er^{3+} ions can directly absorb the pump photons. This is shown in the inset, which shows the pump wavelength dependence of the Er^{3+} luminescence intensity. To clarify the trend, the intensities are normalized

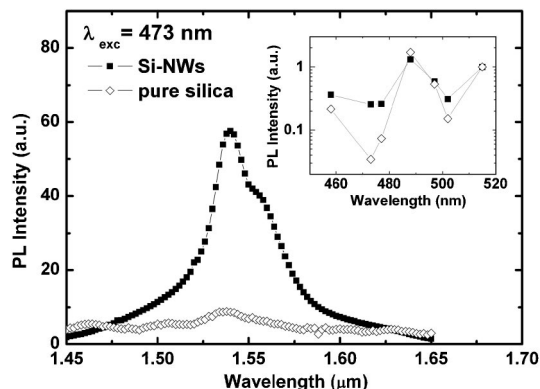


FIG. 2. Room temperature PL spectra of the Si-NWs and pure Er-doped silica film, pumped with the wavelength of 473 nm. The inset shows the wavelength dependence of the PL peak intensities.

to the value at the pump wavelength of 515 nm. The pure silica film without Si-NWs shows appreciable Er^{3+} luminescence only near the pump wavelengths of 488 and 515 nm, reflecting the $^4I_{15/2} \rightarrow ^4F_{7/2}$ and $^4I_{15/2} \rightarrow ^4H_{11/2}$ optical absorption bands of Er^{3+} , respectively. Note that the Er^{3+} luminescence intensity from Si-NWs also displays strong peaks near the pump wavelengths of 488 and 515 nm superimposed on a near-constant background. This indicates that a large fraction of Er^{3+} ions in the sol-gel derived silica film remain inaccessible to carrier-mediated excitation via Si-NWs, which we attribute to the low density of Si-NWs.

Figure 3 shows the effect of temperature on the integrated Er^{3+} PL intensities. The pure silica film was pumped using the 488 nm line of an Ar laser in order to directly excite the Er^{3+} ions. On the other hand, the Si-NWs were pumped using the 477 nm line of an Ar laser, which is not absorbed optically by Er^{3+} ions, in order to probe only those Er^{3+} ions that can be excited via carriers. We observe nearly identical temperature dependence of the Er^{3+} PL intensities, decreasing by less than 10% as the temperature is raised from 25 K to room temperature. The temperature dependence of Er^{3+} luminescence lifetimes are nearly identical, as is shown in the inset. The Er^{3+} luminescence lifetime from the pure silica film decreases from 13.6 to 11 ms as the temperature is raised from 25 to 300 K, while that from the Si-NWs decreases from 8.3 to 6.9 ms.

Given the large diameters of Si-NWs, such complete suppression of thermal quenching of Er^{3+} luminescence can-

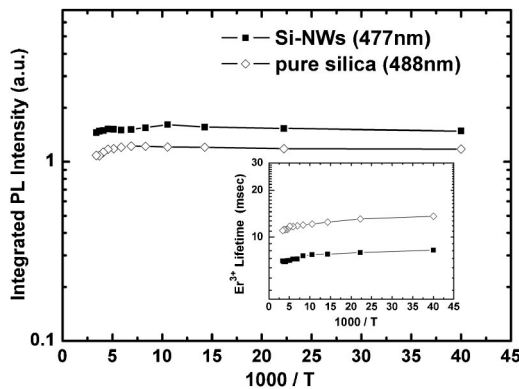


FIG. 3. The temperature dependence of Er^{3+} integrated PL intensities, showing the complete suppression of thermal quenching. The inset shows the temperature dependence of the luminescence lifetimes.

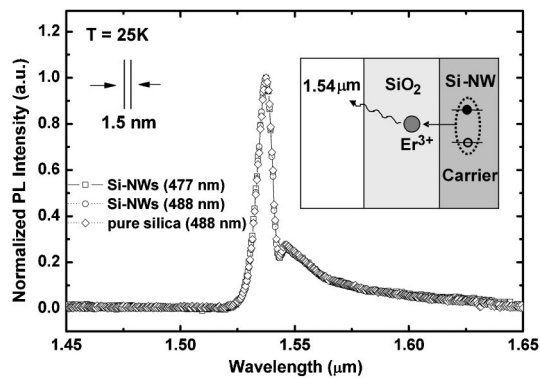


FIG. 4. Normalized PL spectra of pure Er-doped silica (488 nm), with Si-NWs (488 nm) and with Si-NWs (477 nm) at 25 K. The spectra are completely identical within the spectral resolution, indicating that the luminescent Er^{3+} ions are all in silica. The inset shows the schematic description of the proposed Er^{3+} luminescence.

not be due to any quantum effects. In fact, PL investigations of Si-NWs did not show any quantum effects (data not shown). Thus, we conclude that the Er^{3+} ions excited via carriers generated in Si-NWs are actually in the sol-gel derived Er-doped silica film that is coating the Si-NWs, in agreement with previous reports that Er^{3+} ions in a nanometer thin silica shell around Si have both high carrier-mediated excitation efficiency and high Er^{3+} luminescence efficiency irrespective of quantum effects.^{16–18} This conclusion is supported by the low-temperature PL spectra, as shown in Fig. 4. The $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition responsible for the 1.54 μm Er^{3+} luminescence is a parity-forbidden transition that occurs in part due to the effects of the crystal field, and the exact shape and position of the luminescence spectra depend on the chemical and structural environment of Er.¹⁸ However, as Fig. 4 shows, the Er^{3+} PL spectra obtained from the Si-NWs and pure silica film are completely identical irrespective of the pump wavelengths, indicating that the optically excited and carrier-excited Er^{3+} ions are all in the same environment, i.e., in silica.

Since the carrier-Er interaction distance is about a nanometer, the Er^{3+} ions that can be excited via carriers are limited to a thin shell around Si-NWs. Thus, the large enhancement of the Er^{3+} PL intensity observed in Fig. 2 is in part due to the large surface area of the Si-NWs. Note, however, that the pure silica film is in direct contact with the Si substrate whose carriers can, in principle, excite Er^{3+} as well, and yet shows only negligible Er^{3+} luminescence. This is in agreement with previous reports that only negligible carrier-mediated Er^{3+} luminescence could be detected from an Er-doped oxide layer deposited on the surface of a Si substrate,^{7,8,20} and indicates that Si-NWs, even without quantum confinement effects, are much more effective for exciting Er^{3+} ions in an oxide layer on their surface.

The effectiveness of Si-NWs in enhancing the Er^{3+} luminescence can be increased by simply increasing the density of Si-NWs. Furthermore, because the growth of Si-NWs and its coating by sol-gel derived Er-doped silica are performed separately, the two processes can be optimized separately. Indeed, the Er^{3+} luminescence lifetime of 11 ms is as

high as the values reported from Er-doped silica-based waveguide amplifiers²¹ indicating the high quality of the sol-gel derived silica film. Given the identical temperature dependence of the Er^{3+} luminescence lifetime, the reduction of the Er^{3+} luminescence lifetime by Si-NWs is attributed to the effect of increased effective refractive index²² rather than any degradation of the quality of sol-gel derived silica film. Therefore, the results indicate that by using sol-gel derived Er-doped silica to optically activate Si-NWs, we can simultaneously achieve the ease of carrier injection, high carrier-mediated Er^{3+} excitation efficiency, and high Er^{3+} luminescence efficiency in a thick, easily produced film with a very high areal density of Er^{3+} ions, thus providing a promising material platform for Si photonics.

In conclusion, we have investigated optical activation of Si nanowires by spin-coating them with a sol-gel derived Er-doped silica film. Such Er-activated Si nanowires display strong Er^{3+} luminescence, excited via carriers in Si nanowires, yet comparable to pure silica in luminescence efficiency.

This work was supported in part by NRL project by MOST in Korea.

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