

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

Kiseok Suh¹, Oun-Ho Park², Byeong-Soo Bae², Jung-Chul Lee³, Heon-Jin Choi⁴, Jung H. Shin¹

¹Department of Physics, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu, Daejeon, Korea

²Department of Materials Science and Engineering, KAIST, 373-1 Guseong-dong, Yuseong-gu, Daejeon, Korea

³Materials science and Technology Division, Korea Institute of Science and Technology (KIST), P.O. Box 131, Cheongryang, Seoul 130-650, Korea

⁴Department of Ceramics, Yonsei University, Seoul 120-749, Korea

ABSTRACT

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 new material platform for Si-based photonics.

INTRODUCTION

Efficient Si-based light emitting material has been attracting much interest because of its potential application in photonics with Si technology[1]. In particular, Er-doping of Si material has great importance due to their Er³⁺ intra-4f emission at 1.54 μm, the standard wavelength for telecommunications. After the initial report[2], Er-doped Si light emitting diodes (LEDs) operating at room temperature were demonstrated with good electrical properties. However, the luminescence efficiencies were quite poor due to their intrinsic Auger- and temperature quenching of Er³⁺ luminescence[3]. On the other hand, excellent optical properties were obtained by using silicon-rich-silicon-oxide (SRSO), which consists of nanocluster Si (nc-Si) embedded

inside an SiO₂ matrix[4]. Although optical gain[5] as well as efficient LED[6] have been demonstrated, SiO₂ matrix makes current injection difficult, resulting in requirement of high voltages or thin SRSO layers for LED operation. 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, since electronic devices based on Si-NWs operating at voltages of less than 5 volts were demonstrated[7].

However, due to the limited solubility of Er in Si, Er segregates at the interface during growth of Er-doped Si, and can lead to defective growth. Indeed, 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[8]. On the other hand, there have been reports that the Er³⁺ can be excited by carriers over a distance of a nm, and that the optimum location for Er³⁺ is not inside Si, but in the nm-thin oxide shell right next to Si[9]. 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 paper, we report on the results of such optical activation of Si-NWs using sol-gel derived Er-doped silica.

EXPERIMENTAL DETAILS

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[10]. During growth, H₂ and Ar gases were introduced into the tube at a flow rate of 100 sccm, respectively. SiCl₄ was introduced into the tube 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 900 °C. Er-doped silica sol-gel solution was prepared by first hydrolyzing tetraethylorthosilicate (TEOS, Aldrich) in a 0.05 M HCl aqueous solution with ethanol as the cosolvent. Er-doping was achieved with ErCl₃·6H₂O (Aldrich) with a ErCl₃·6H₂O /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 RT for 1 day. The solution was spin coated on the Si-NW grown Si wafers at 1000 rpm for 30 sec, and annealed at 450 °C for 7 hours in a flowing N₂/O₂ environment to remove volatile organic compounds. Finally, a rapid thermal anneal at 950 °C for 5 min in a flowing N₂/O₂ environment was used to activate erbium. The silica layer thickness was about 5 μ m. 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 μ m in this case due the absence of Si-NWs. The Er³⁺ photoluminescence (PL) spectra were measured using an Ar laser, a grating monochromator, a thermo-electrically cooled InGaAs detector, and the standard lock-in technique. Low temperature

PL spectra were measured using a closed-cycle helium cryostat, and Er^{3+} PL decay traces were measured using a digitizing oscilloscope.

DISCUSSION

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-NW are not normal to the substrate, however. They lie at an angle of about 60 degrees from the surface normal. Figure 1 (b) shows an 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. Note, however, that portions of Si-NWs protrude from the silica layer, providing continuous current paths to the underlying Si substrate. Some macroscopic cracks due to shrinkage of the sol-gel derived film during drying and annealing can also be observed[11]. It should be pointed out here that 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 and 488 nm line of an Ar laser. The intensities are normalized by the peak intensities obtained when pumped with the 488 nm. The 473 nm line was chosen because it is absorbed only by Si-NWs and not directly by Er^{3+} ions. Er^{3+} ions can absorb the photon with the wavelength of 488 nm.

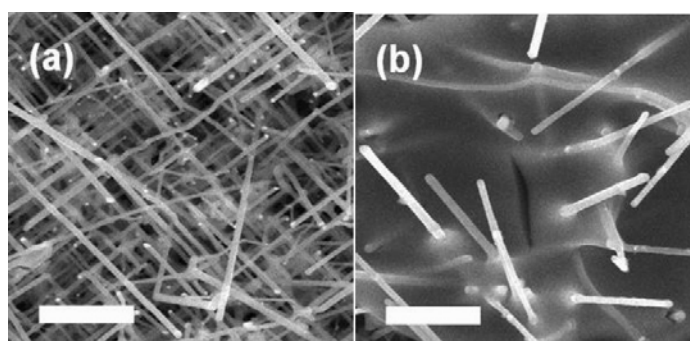


Figure 1. SEM images of (a) as-grown Si-NWs and (b) Er-doped, sol-gel-derived silica film coated on Si-NWs. Scale bar represents 2 μm .

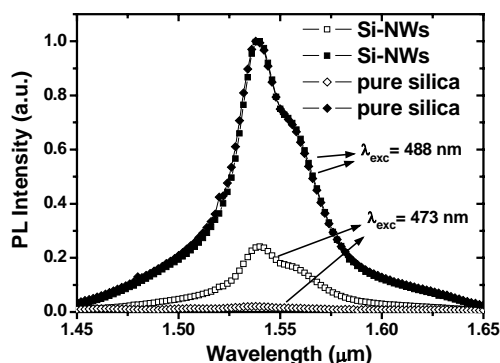


Figure 2. Room temperature PL spectra of the Si-NWs and pure Er-doped silica film

Unlike pure silica film, Si-NWs pumped with the 473 nm show strong Er^{3+} luminescence at 1.54 μm , indicating energy transfer from carriers in Si-NWs to Er^{3+} ions i.e., Er^{3+} excitation occurs via carriers only, and represents an accurate simulation of the situation under current injection.

Figure 3 shows the pump wavelength dependence of the Er^{3+} luminescence intensity. The intensities are normalized 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 $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$ and $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ 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 silica film remain inaccessible to carrier-mediated excitation via Si-NWs, which we attribute to the low density of Si-NWs.

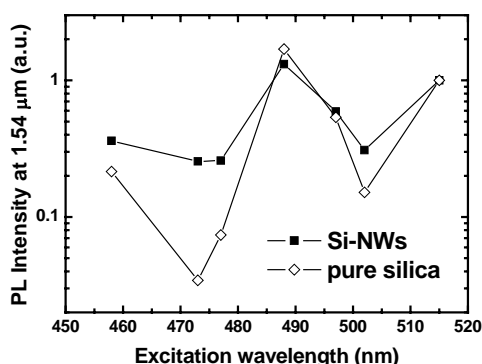


Figure 3. The pump wavelength dependence of the Er^{3+} luminescence intensity

Figure 4 (a) 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 from Si-NWs and pure silica film 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 msec as the temperature is raised from 25 to 300 K, while that from the Si-NWs decreases from 8.3 to 6.9 msec.

Given the large diameters of Si-NWs, such complete suppression of thermal quenching of Er^{3+} luminescence cannot be due to any quantum effects. In fact, PL investigations of Si-NWs did not show any quantum effects (data not shown). Yet Er^{3+} luminescence from bulk, crystalline Si is known to undergo severe temperature quenching[3]. 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 nm-thin silica shell around Si have both high carrier-mediated excitation efficiency and high Er^{3+} luminescence efficiency irrespective of quantum effects[12].

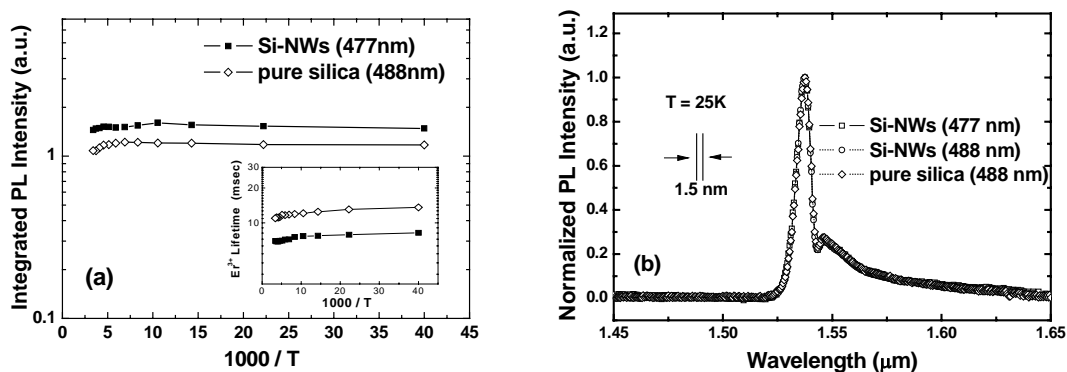


Figure 4. (a) The temperature dependence of Er^{3+} integrated PL intensities, showing the complete suppression of thermal quenching. The inset shows the temperature dependence of the luminescence lifetimes. (b) Normalized PL spectra of pure Er-doped silica (488 nm), with Si-NWs (488 nm) and with Si-NWs (477 nm) at 25 K.

This conclusion is supported by the low-temperature PL spectra (Figure 4 (b)). 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[13]. However, 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.

CONCLUSIONS

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 efficiently, yet comparable to pure silica in luminescence efficiency, showing promise of fabricating LEDs based on Si operating at low voltages.

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