

Large-scale fabrication of single-phase Er_2SiO_5 nanocrystal aggregates using Si nanowires

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(Received 6 July 2006; accepted 9 October 2006; published online 27 November 2006)

Single-phase Er_2SiO_5 nanocrystal aggregates were produced on a large scale using Si nanowire (Si-NW) arrays as templates. A dense array of Si-NWs was grown by vapor-liquid-solid mechanism using Au catalyst on Si (111) substrate. Afterwards, $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved ethanol solution was spin coated and annealed first at 900 °C for 4 min in a flowing N_2/O_2 environment and then at 1200 °C in a flowing Ar environment for 3 min. X-ray diffraction, scanning electron microscope, and high-resolution transmission electron microscope measurements indicate that due to the use of Si-NWs, such a short annealing procedure is sufficient to completely transform the Er-coated Si-NWs into a thick, large-area aggregate of pure, single-phase to Er_2SiO_5 oxyorthosilicate nanocrystals. The crystalline nature of Er_2SiO_5 film and the loose nature of the aggregate result in an atomlike Er^{3+} spectrum with a very narrow luminescence linewidth at 1.53 μm , which together with a complete lack of temperature quenching of Er^{3+} luminescence and a high Er concentration indicate a viability of this method to fabricate efficient, high-gain Si-based optical material for Si photonics. © 2006 American Institute of Physics. [DOI: [10.1063/1.2393162](https://doi.org/10.1063/1.2393162)]

There is a strong and growing interest in developing Si photonics that can integrate the fast, lossless information carrying capacity of photonics with Si integrated circuit technology to overcome the impending “interconnect bottleneck.”¹ In particular, a great effort has been made in developing a Si-based light source, especially a laser, that can overcome the inherent limitation of the indirect band gap of Si.^{1,2} Among the many possible ways of obtaining light emission from Si,^{3–5} using the rare earth ion Er^{3+} as an optical dopant has attracted a special attention because of its ability to provide light at 1.5 μm that is compatible not only with optical telecommunication but also with silicon-on-insulator based Si microphotonic devices.^{5,6} Furthermore, Er doping has a history of proven success in providing optical gain and lasing when doped into silica fiber amplifiers.⁷

The intra- $4f$ transition of Er^{3+} that gives rise to the 1.5 μm luminescence is parity forbidden and occurs due to the effects of the crystal field surrounding Er^{3+} ions. This leads to long luminescence lifetimes and, when doped into an amorphous host such as silica, large inhomogeneous broadening of the atomic luminescence peak that allow for low-noise, broadband amplification capability of EDFAs. Unfortunately, the same qualities can lead to severe limitations for its applicability for Si photonics that requires a large optical gain in a limited wavelength range from a micrometer-sized volume, since the combination of long luminescence lifetimes and a broad luminescence peak results in a low gain cross section at a particular wavelength. Increasing the gain requires a very high Er concentration, but the concentration of optically active Er that can be doped into a host material without clustering is limited, even for an amorphous host such as silica.^{8,9} Another way of increasing

the gain cross section per wavelength is reducing the inhomogeneous broadening of Er^{3+} luminescence by using a crystalline host matrix, but even in that case, controlling the location of Er^{3+} ions down to atomic levels is difficult.¹⁰

A rather interesting alternative to Er doping that can overcome these difficulties is to raise the Er concentration so high that a stable, Er rich crystalline phase can form. In particular, crystalline rare earth oxyorthosilicates ($R_2\text{SiO}_5$) provide a combination of a very high concentration of optically active rare earth ions in a stable material. Furthermore, since there are only two possible sites¹¹ for rare earth ions that are separated by either oxygen atoms or SiO_4 tetrahedra, the rare earth ions are expected to suffer very little inhomogeneous broadening, as well as be dispersed on an atomic scale as not to suffer from clustering or segregation. Indeed, there have been many reports of using various combination of $R_2\text{SiO}_5$ to realize efficient solid-state lasers.¹²

Such lasers, however, used bulk crystals grown from a crucible and therefore are not compatible with integrated photonics that require materials in a thin-film form. Recently, sharp luminescence was reported from an Er_2SiO_5 thin film formed by sol-gel technique, but only after prolonged annealings at temperatures in the excess of 1200 °C that render it unsuitable for optoelectronic integration.¹³ In this letter, we report on producing single-phase Er_2SiO_5 nanocrystal aggregates on a large scale using $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved ethanol solution and Si nanowire (Si-NW) arrays as templates. The nanometer-scale size, high aspect ratio, and the large surface area of Si-NWs enable formation of a thick, large-area aggregate of pure, single-phase to Er_2SiO_5 nanocrystals after a rapid thermal annealing of only 3 min at 1200 °C. The crystalline nature of Er_2SiO_5 film and the loose nature of the aggregate result in sharp, atomlike Er^{3+} spectrum with a very narrow luminescence linewidth at 1.53 μm , which together with a complete lack of temperature quenching of Er^{3+} lumi-

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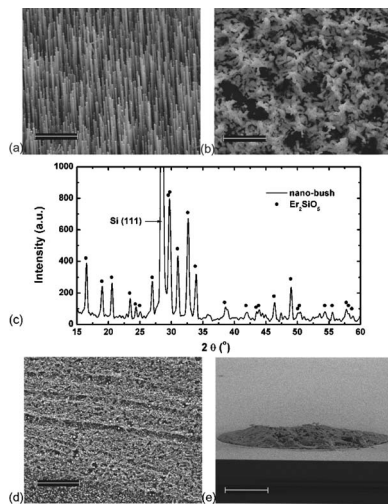


FIG. 1. SEM images of (a) as-grown Si-NWs and (b) fabricated nanobush after spin coating the Si-NWs with Er solution and annealing. (c) XRD spectrum of fabricated nanobush well agrees with the JCPDS powder diffraction file of Er_2SiO_5 indicated by circles. Large area SEM image of (d) fabricated Er_2SiO_5 . Er_2SiO_5 was formed uniformly across the wafer. Large area SEM image of (e) spin coating the blank Si wafer with Er solution and annealing. Randomly dotted with $\sim 10 \mu\text{m}$ sized, irregularly shaped clumps were fabricated. Note that the use of Si-NWs allows large-scale fabrication of Er_2SiO_5 uniformly. Scale bar of (a), (b) represents $2 \mu\text{m}$ and that of (d), and (e) represents $20 \mu\text{m}$.

nescence and a high Er concentration indicate a viability of this method to fabricate efficient, high-gain Si-based optical material for Si photonics.

Si-NWs are grown by vapor-liquid-solid mechanism¹⁴ using Au catalyst deposited on Si (111) substrates by sputtering. During growth, SiCl_4 was introduced into growth furnace held at 900°C by bubbling H_2 carrier gas through liquid SiCl_4 held at 0°C at a flow rate of 1–10 SCCM (SCCM denotes cubic centimeter per minute at STP). Ar and H_2 gases were also introduced into the furnace at a flow rate of 100 SCCM, respectively. The growth time was 30 min. After Si-NW growth, an Er solution prepared by dissolving $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (3.0 g) into ethanol (8.2 g) was spin coated on the Si-NWs at 4000 rpm for 1 min. Following spin coating, a rapid thermal annealing at 900°C for 4 min in a flowing N_2/O_2 environments is followed by another annealing at 1200°C for 3 min in a flowing Ar. The structure of the resulting silicate film was analyzed using θ - 2θ x-ray diffraction (XRD) and transmission electron microscopy (TEM). Photoluminescence (PL) spectra were measured using an Ar laser, monochromator, a thermoelectrically cooled InGaAs detector, and the standard lock-in technique. The low-temperature measurements were made using a closed cycle He cryostat.

Figure 1(a) shows a scanning electron microscope (SEM) image of as-grown Si-NWs, showing a dense array of vertically aligned Si-NWs. The diameter and the lengths of the Si-NWs were about 100 nm and $\sim 10 \mu\text{m}$, respectively, with a Si-NW density of $1.4 \times 10^9 \text{ cm}^{-2}$. Figure 1(b) shows the SEM image of the Si-NWs after spin coating the Er solution and annealing. We find that Si-NWs have disappeared and instead observe a “nanobush” of roughly spherical grains. Figure 1(c) shows the θ - 2θ XRD spectrum of the transformed nanobush. From the position of the diffraction peaks, we identify the nanobush to consist of nearly pure Er_2SiO_5 , which is a stable phase¹⁵ in the Er_2O_3 - SiO_2 system with a monoclinic symmetry of space group $P2_1/c$.¹¹ Given

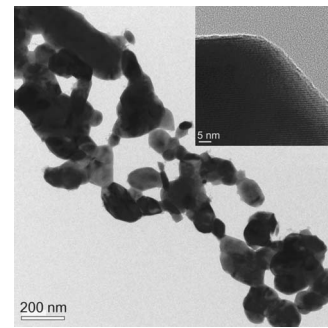


FIG. 2. Bright field TEM image of fabricated Er_2SiO_5 . The size of nanocrystal grains is about 50–200 nm in diameter. The inset shows high-resolution TEM image of Er_2SiO_5 indicating the single crystalline nature of Er_2SiO_5 nanocrystal.

the number density of Si-NWs and assuming that all Si-NWs were consumed to form Er_2SiO_5 , we estimate that there is $\sim 0.35 \text{ mg}$ of $\text{Er}_2\text{SiO}_5/\text{cm}^2$.

It should be noted here that the use of dense, thick array of Si-NWs is critical for such controlled, large-scale formation of pure Er_2SiO_5 . This is shown in Figs. 1(d) and 1(e), which show the large-area SEM images of Si-NWs and a blank Si wafer, respectively, that were spin coated with the Er solution and annealed. We find that for Si-NWs, formation of Er_2SiO_5 is uniform across the wafer—indeed, it was this large-scale formation of a thick, uniform film that enabled the XRD analysis. In the case of the blank wafer, on the other hand, we observe mostly unreacted Si surface randomly dotted with $\sim 10 \mu\text{m}$ sized, irregularly shaped clumps that were determined to be mixture of various phases of Er_2O_3 - SiO_2 system. We attribute this difference to the nanometer-sized diameter and large surface area of Si-NWs, as they are much better suited for chemical reaction and atomic transport between crystalline Si and Er solution that are necessary for the formation of Er_2SiO_5 . In fact, the annealing procedure required to form Er_2SiO_5 with Si-NWs is much less severe than even that for sol-gel derived Er_2SiO_5 , which requires 20 min annealing at 1250°C even though the reactants are mixed on an atomic scale.¹³ It is also possible that Si-NWs trap the Er solution much better and more uniformly than a blank Si wafer can.

Figure 2 shows the TEM image of fabricated Er_2SiO_5 . The TEM samples were prepared by simply ultrasonically breaking up the as-grown Er_2SiO_5 film in ethanol to break it up, as the film consisted of loose aggregates of Er_2SiO_5 nanocrystals that are about 50–200 nm in diameter. Each nanocrystal grains are randomly oriented, but are single crystalline, as is shown by the high-resolution TEM image shown in the inset. Note that we do not see any resemblance to original Si-NWs, indicating that they break up during the formation Er_2SiO_5 , most likely due to the large differences in crystal structure and lattice parameters between Si and Er_2SiO_5 .

Figure 3 shows the PL spectra of the Er_2SiO_5 film, obtained using the 488 nm line of an Ar ion laser to optically excite the $^4I_{15/2} \rightarrow ^4F_{7/2}$ transition of Er^{3+} ions. As is shown in the inset, very little Er^{3+} PL could be observed when the film was pumped off-resonance at 477 nm, indicating that host sensitization does not occur. We find that at low temperature, the PL spectrum is nearly atomlike with a series of sharp peaks. The width of the central peak at 1530 nm is limited by the system resolution, which was 1.5 nm. Even at room temperature, the central peak dominates the PL spectrum with full width at half maximum (FWHM) of less than

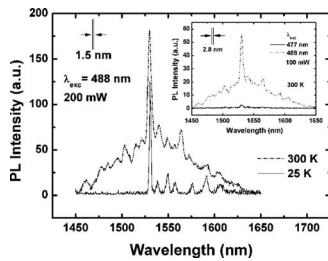


FIG. 3. PL spectra of the Er_2SiO_5 film using the 488 nm line of an Ar laser at room temperature and 25 K show atomically sharp luminescence of Er^{3+} . The width of the central peak at 1530 nm is about 4.5 nm at room temperature and about 1.5 nm at 25 K. The inset shows the PL spectra of the Er_2SiO_5 film using the 477 and 488 nm lines of an Ar laser. Very little Er^{3+} PL was observed using 477 nm (off-resonance) indicating that the direct optical absorption is the dominant excitation process for Er^{3+} .

4.5 nm or 3 meV. It should be noted here that the spectra are not intentionally offset—the Er^{3+} PL intensity *increases strongly* as the temperature is raised. The peak intensity increases by 50%, while the integrated PL intensity increases more than sevenfold. At this moment, it is not clear why this should be so. It may be that more transitions become available as the temperature is raised, as the increase in the width of the PL spectrum indicates. It is also possible that with increasing temperature, the transition rate from the higher-lying states to the first excited state responsible for the 1.5 μm transition increases. We note that such a sharp, atom-like luminescence is not an inevitable by-product of using a crystalline material. In many cases where a polycrystalline thin film is used, the presence of grain boundaries and strain often results in a very large inhomogeneous broadening not only from Er-doped polycrystalline Al_2O_3 (Ref. 9) but also from pure Er_2O_3 as well.¹⁶ In contrast, no such inhomogeneous broadening is observed from the Er_2SiO_5 film investigated here as it consists of loose aggregate of high quality nanocrystal grains.

The data presented so far demonstrate clearly that by using Si-NWs, it is possible to fabricate Er_2SiO_5 thin films with a modest thermal budget, and also highlight the difference between this letter and previous reports on infiltration of Si nanostructures with Er solution^{17–19} that aimed at producing either Er-doped Si or Si nanostructure sensitized, Er-doped silica. These efforts, while successful, provided a low active Er concentration and a broad Er^{3+} luminescence linewidth unless put into a microcavity.¹⁸ The present method, on the other hand, simultaneously achieves a very high optically active Er concentration ($2 \times 10^{22} \text{ cm}^{-3}$), very narrow luminescence linewidth, and complete suppression of temperature quenching Er^{3+} luminescence, conditions which would allow, in principle, a very high-gain coefficient. The value of emission cross section for Er^{3+} ions in Er_2SiO_5 is not well known. However, given that the peak emission cross section for Er^{3+} in polycrystalline Al_2O_3 with a FWHM of 55 nm is $6 \times 10^{-21} \text{ cm}^2$, the maximum possible gain from Er_2SiO_5 would be in the excess of at least 120 cm^{-1} —albeit only within a wavelength window of less than 4.5 nm.

In reality, the maximum obtainable gain at 1.53 μm would be limited by nonlinear effects such as upconversion. On the other hand, it had been reported that upconversion in crystalline phase of erbium oxides is strongly reduced compared to that from silica due to the atomic-scale dispersion of Er.¹⁶ The granular nature of the film can lead to strong scattering as well. Such scattering losses, however, can be alle-

viated by infiltrating the film with index-matched polymer, as had been shown for silica nanospheres.²⁰ Given that the refractive index²¹ of Er_2SiO_5 is 1.825, such a material would have a further advantage of enabling very compact photonic circuits on silica. Furthermore, since the grains are nanometer sized and easily separated, they can be incorporated into small pores of optical nanostructures such as photonic crystals and slot waveguides,²² whose small sizes require a high-gain coefficient. Finally, we note that the PL spectrum shown in Fig. 3 is nearly identical to that reported by Isshiki *et al.*,²³ suggesting that the unidentified Er–Si–O compound that they observed Er_2SiO_5 .

In conclusion, we have fabricated thick Er_2SiO_5 film using silicon nanowires spin coated with Er solution. Use of silicon nanowires allowed large-scale fabrication of loose aggregates of high quality Er_2SiO_5 nanocrystals, resulting in atomically sharp luminescence even at room temperature. Furthermore, the films do not show any temperature quenching of Er^{3+} luminescence, which together with the high Er concentration and sharp luminescence spectrum indicate promise of using this material for compact, high-gain silicon-based light source.

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

¹See, for example, *Towards the First Silicon Laser*, NATO Science Series II: Mathematics, Physics and Chemistry (Springer, New York, 2003), p. 93.

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