Large-scale fabrication of single-phase Er$_2$SiO$_5$ nanocrystal aggregates using Si nanowires

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Single-phase Er$_2$SiO$_5$ 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, ErCl$_3$·6H$_2$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$_2$SiO$_5$ oxyorthosilicate nanocrystals. The crystalline nature of Er$_2$SiO$_5$ 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]

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.” In particular, a great effort has been made in developing Si-based light source, especially a laser, that can overcome the inherent limitation of the indirect band gap of Si. Among the many possible ways of obtaining light emission from Si, 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 microphotic devices. Furthermore, Er doping has a history of proven success in providing optical technology to overcome the impending “interconnect bottleneck” by using a crystalline host matrix, but even in that case, controlling the location of Er$^{3+}$ ions down to atomic levels is difficult.

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$_2$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 sites 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 to not suffer from clustering or segregation. Indeed, there have been many reports of using various combination of R$_2$SiO$_5$ to realize efficient solid-state lasers.

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$_2$SiO$_5$ 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. In this letter, we report on producing single-phase Er$_2$SiO$_5$ nanocrystal aggregates on a large scale using ErCl$_3$·6H$_2$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$_2$SiO$_5$ nanocrystals after a rapid thermal annealing of only 3 min at 1200 °C. The crystalline nature of Er$_2$SiO$_5$ 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$^{3+}$ luminescence due to the effects of the crystal field surrounding Er$^{3+}$ ions. This leads to long luminescence lifetimes 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. Another way of increasing

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with a Si-NW density of 1.4/cm².

Peaks, we identify the nanobush to consist of nearly pure liquid SiCl₄ held at 0 °C at a flow rate of 1–10 SCCM with a monoclinic symmetry of space group P2₁/c. Figure 1 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 ~10 μm, respectively, with a Si-NW density of 1.4 × 10⁶ 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 Er₂SiO₅, which is a stable phase in the Er₂O₃–SiO₂ system with a monoclinic symmetry of space group P2₁/c. Given the number density of Si-NWs and assuming that all Si-NWs were consumed to form Er₂SiO₅, we estimate that there is ~0.35 mg of Er₂SiO₅/cm².

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 Er₂SiO₅. 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 Er₂SiO₅ 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 ~10 μm sized, irregularly shaped clumps that were determined to be mixture of various phases of Er₂O₃–SiO₂ 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 Er₂SiO₅. In fact, the annealing procedure required to form Er₂SiO₅ with Si-NWs is much less severe than even that for sol-gel derived Er₂SiO₅, which requires 20 min annealing at 1250 °C even though the reactants are mixed on an atomic scale. 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 Er₂SiO₅. The TEM samples were prepared by simply ultrasonication of the as-grown Er₂SiO₅ film in ethanol to break it up, as the film consisted of loose aggregates of Er₂SiO₅ 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 Er₂SiO₅, most likely due to the large differences in crystal structure and lattice parameters between Si and Er₂SiO₅.

Figure 3 shows the PL spectra of the Er₂SiO₅ film, obtained using the 488 nm line of an Ar ion laser to optically excite the F₄(15/2)→F₇/₂ transition of Er³⁺ ions. As is shown in the inset, very little Er³⁺ 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 10 nm.
FIG. 3. PL spectra of the Er$_2$SiO$_5$ 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$_2$SiO$_5$ 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 PL spectrum indicates. It is also possible 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 more transitions become available as the temperature is raised, as the increase in the width of the PL spectrum indicates.

The data presented so far demonstrate clearly that by using Si-NWs, it is possible to fabricate Er$_2$SiO$_5$ 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 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 until put into a microcavity. The present method, on the other hand, simultaneously achieves a very high optically active Er concentration (2 × 10$^{22}$ 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$_2$SiO$_5$ is not well known. However, given that the peak emission cross section for Er$^{3+}$ in polycrystalline Al$_2$O$_3$ with a FWHM of 55 nm is 6 × 10$^{-21}$ cm$^2$, the maximum possible gain from Er$_2$SiO$_5$ would be in the excess of at least 120 cm$^{-1}$—albeit only within a wavelength window of less than 4.5 nm.

In conclusion, we have fabricated thick Er$_2$SiO$_5$ film using silicon nanowires spin coated with Er solution. Use of silicon nanowires allowed large-scale fabrication of loose aggregates of high quality Er$_2$SiO$_5$ 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.

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