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Green and Red Emissions at Room Temperature on Er-Doped GaN Submicrometer Rods Synthesized by a Simple Chemical Vapor Deposition Technique

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Er-doped GaN submicron rods have been synthesized on silicon (001) by the direct reaction of gallium and ammonia in a CVD system. Green and red emissions at room temperature coming from the rods with excitation below the energy of the bandgap of the semiconductor have been recorded.

Introduction

The photoemission generated by lanthanide (Ln) ions in Ln-doped semiconductors has been limited at room temperature principally because of two factors: (i) the low solubility of Ln in semiconductors, and (ii) the severe temperature quenching that the photoemission suffers at room temperature in these materials.[1] This thermal quenching has been reported to decrease as the bandgap of the semiconductor increases.[2] Thus, wide bandgap semiconductors are more attractive as hosts for Ln ions than traditional smaller bandgap semiconductors such as Si or GaAs.

Gallium nitride (GaN) is a wide bandgap semiconductor with important applications in the fabrication of UV and blue-light emitters, detectors, high-speed field-effect transistors (FETs), and optoelectronic high-power/high-temperature devices.[3] The direct bandgap of GaN makes it of particular interest as a host for Ln ions. This may allow the electrical excitation of Ln ions, through impact excitation of hot carriers from the semiconductor with the Ln ions or as a result of nearby electron–hole recombination, generating a nearly ideal optical emission that can be properly amplified.[4]

Because of the importance of the 1.5 μm emission generated by erbium (Er) for optical communications, this ion has been the main Ln doping ion studied in semiconductors, including GaN. Recently, strong green (537 and 558 nm) and infrared (1.54 μm) luminescence at room temperature have been recorded on Er-doped GaN thin layers[5] and powders[6] after pumping at 325 and 496.5 nm, respectively. These results brings additional interest to further extend the already wide field of applications of this semiconductor with applications in optics, photonics, and telecommunications, optical amplifiers, optical storage devices, full color displays, and near-infrared light-emitting optical sources.[4,7]

During the past decade, much effort has been directed toward the synthesis of one-dimensional GaN submicrometer and nanostructures (namely, nanowires, nanorods, and nanotubes) with means of controlling their diameters[8] and probing their functionality in different devices such a light-emitting diodes,[9] diode lasers,[10] and FETs.[11] Incorporating Er in these GaN one-dimensional structures may enable new functional devices through hybrid integration with a variety of other passive and active optical materials. Furthermore, as GaN can withstand high temperatures, active structures compatible with complementary metal oxide semiconductor (CMOS) technology could be fabricated if Er-doped GaN one-dimensional submicrometer and nanostructures are integrated in silicon (001) substrates.[12]

In this paper, we present the successful synthesis of Er-doped GaN submicrometer rods deposited on silicon (001) substrates by a catalyst-assisted chemical vapor deposition (CVD) technique.[8] Other authors have proven that this technique is also useful for doping GaN with Mg to create *p*-type GaN nanowires,[13] and with Mn to induce magnetic

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properties in these one-dimensional nanostructures.[14] We have been able to identify several optical absorption bands of Er in these rods, including the hypersensitive bands. Confocal microscopy characterization has revealed emission at room temperature from as-synthesized Er-doped GaN submicrometer rods in the 495–540 and 640–900 nm regions after excitation at 488 and 543 nm, respectively, always at an energy below the bandgap of the semiconductor. Although Er has been incorporated in other $ErSi_{2-x}$,[15] Si,[16] and ZnO[17] nanowires, this is the first time, to the best of our knowledge, that visible emission is reported from such one-dimensional submicrometer structures.

Experimental Section

Er-doped GaN submicrometer rods were prepared via metal-catalyzed CVD, in a horizontal tubular furnace using gallium metal (99.99999%), ammonia (99.999%), and erbium metal (99.9%, 325 mesh) as the Ga, N, and Er sources, respectively. The silicon (001) substrates were cleaned in hot acetone and hot ethanol for 10 min and then dipped in a solution 0.01 M $Ni(NO_3)_2$ in ethanol, as nickel is the metal catalyst used in this process. The distance between the Ga source and the substrate was always 1.2 cm. The Er source was located downstream in the furnace with respect to the Ga source, before the Si substrate. The molar ratio between Ga and Er was 4:1 in all the experiments. Several locations were tested for the Er source. However, as the vapor pressure of Er is very low at the temperature of the reaction ($\sim 7.5 \times 10^{-6}$ Torr at 800 °C and $\sim 1.0 \times 10^{-4}$ Torr at 900 °C[18]), we put the Er source in contact with the silicon substrate to ensure sufficient flow of atoms to its surface. The quartz tube of the furnace was degassed to a vacuum pressure of 1×10^{-2} Torr. Ammonia gas was introduced at a flow rate ranging from 50 to 75 sccm. In all the experiments, the total pressure at the downstream end of the furnace was kept at 15 Torr with no additional carrier gas except ammonia used. Upon heating to a preset temperature between 1073 and 1173 K, the system was kept at this temperature for 1 h, and then cooled to room temperature after the flow of NH_3 was stopped.

Er-doped GaN submicrometer rods were visualized by scanning electron microscopy (SEM) in a LEO 1550 SFEG-SEM equipped with a Robinson BackScatter detector and by transmission electron microscopy (TEM) in a Phillips CM12 TEM microscope. Their chemical composition was analyzed by energy-dispersive X-ray fluorescence (EDAX).

Optical absorption of Er-doped GaN rods was studied at room temperature in a Varian Cary 500 Scan spectrophotometer. To perform these measurements, we dispersed the Er-doped GaN submicrometer rods in ethanol and homogenized them with ultrasounds. A quartz cell, with dimensions of 5 mm × 5 mm and 1 mm thick, was filled with the dispersion of Er-doped GaN rods in ethanol and introduced in the sample chamber of the spectrophotometer. We used an aperture to ensure no obscuration in the absorption measurements by the edges of the quartz cell.

A Nikon Eclipse TE 2000-E confocal microscope was used to study luminescence emission coming from the Er-doped GaN rods after excitation at 488, 543, and 633 nm. Excitation wavelengths were provided by argon (488 nm) or He−Ne (543 and 633 nm) lasers attached to the microscope. Emission was recorded with a Hamamatsu R928 photomultiplier tube to which several filters have been attached with windows in the 495–540, 560–610, and 640–900 nm ranges of the electromagnetic spectrum.

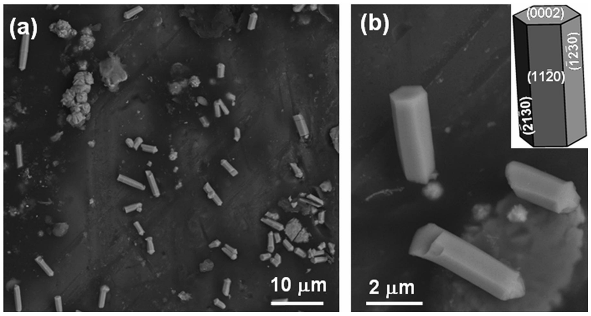

Figure 1. Scanning electron micrographs of the Er-doped GaN submicrometer rods grown at 1073 K with a flow of NH_3 of 75 sccm. (a) Low-magnification image showing several Er-doped GaN rods dispersed onto the Si substrate, and (b) high-magnification image of three of those Er-doped GaN rods, one of them still standing on the Si substrate, and schematic representation of its morphology.

Results and Discussion

SEM images of the GaN submicron rods obtained on the silicon substrate at 1073 K using a flow rate of ammonia of 75 sccm are shown in Figure 1. Figure 1a shows a low magnification image in which several GaN rods can be seen dispersed onto the silicon substrate. Figure 1b shows a high-magnification image of three of those GaN rods, one still standing onto the Si substrate, whereas the other two are lying on it. The submicrometer rods exhibited a hexagonal cross-section with diameters ranging between 500 and 1000 nm, and lengths up to 10 μm. The observed hexagonal cross section was a clear indication that the rods are wurtzite GaN growing along the *c* crystallographic direction. Pyramidal tips are observed at the end of the rods with a size less than 100 nm in diameter, as can be seen in the magnification of some of those rods shown in Figure 1b.

Energy-dispersive X-ray fluorescence (EDAX) was used to characterize chemically the Er-doped GaN submicrometer rods. A typical spectrum of one of those GaN rods is shown in Figure 2. This spectrum was recorded on an isolated and thick submicrometer rod, also shown in the figure, to ensure that the X-rays generated are coming only from the GaN rod. In addition to the peaks of Ga and N, expected for the GaN rods, two peaks corresponding to Er and a peak corresponding to oxygen can be seen in the spectrum. Also, a peak corresponding to gold is observed that is due to the coating layer used to characterize the samples by SEM. No precipitates can be seen on the surface of the rods and no layers with different contrast can be detected on the SEM images. The oxygen peak may originate from the thermal decomposition of the catalyst. The effect of the presence of oxygen on the Er luminescence in GaN has been the object of controversy, with studies that state a beneficial influence, studies that report no obvious benefit, or even others that

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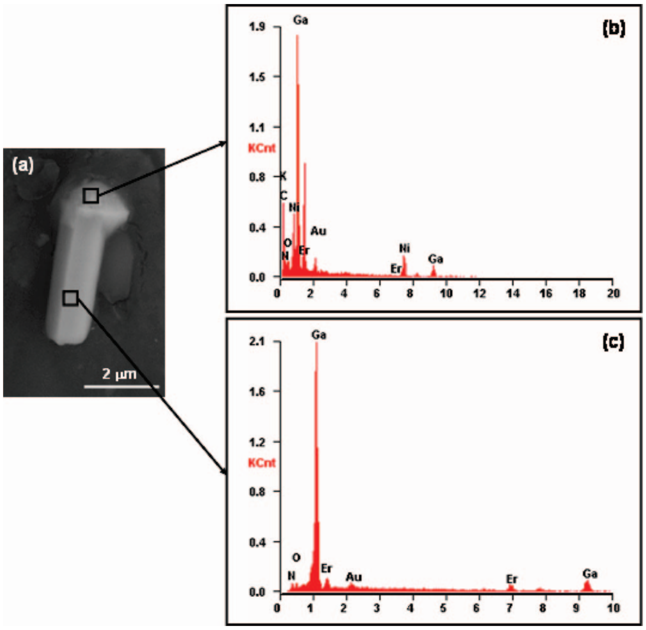

Figure 2. (a) Scanning electron micrograph of an Er-doped GaN submicrometer rod showing a Ni-based cluster attached to one of its ends. (b) Energy-dispersive X-ray fluorescence (EDAX) spectrum of the body of Er-doped GaN rod. (c) EDAX spectrum of the Ni-based cluster attached to the end of the Er-doped GaN rod.

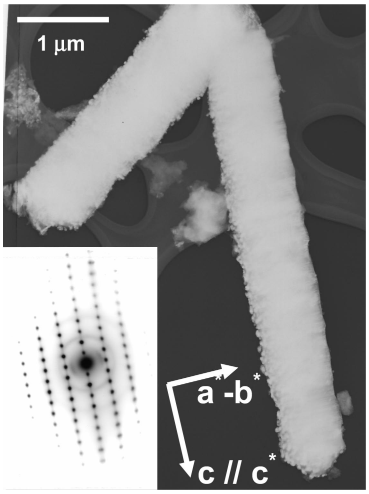

Figure 3. Transmission electron micrograph showing two Er-doped GaN submicron rods. The inset shows the selected area electron diffraction (SAED) pattern recorded along the $\langle 11\bar{2}0\rangle$ zone axis.

claim a negative impact on the emission intensity.[19] The presence of some Ni-based clusters at the end of the rods, as determined by EDAX (see Figure 2), suggests that the growth process of these rods proceeds via a vapor–liquid–solid mechanism (VLS).[8] Semiconductor material or its precursors, including Er, in vapor form are incorporated into the growing rods by means on a droplet of liquid catalyst. The nano or submicrometer droplets, located at the tips of the rods, act as seeds for the growth, thus determining wire diameters.

Figure 3 shows a TEM micrograph of two of these submicrometer rods. The irregularities on the surface of the rods are caused by a thin layer of gold nanoparticles deposited before for SEM characterization. Some of these nanoparticles are evident in the image. One of the rods shows the pyramidal tip already observed by SEM. Figure 3 inset shows the $\langle 11\bar{2}0\rangle$ electron diffraction pattern. All the diffraction peaks in the selected area electron diffraction (SAED) pattern could be indexed according to the wurtzite structure of GaN. This indicates that the Er-doped GaN rods were single crystal.

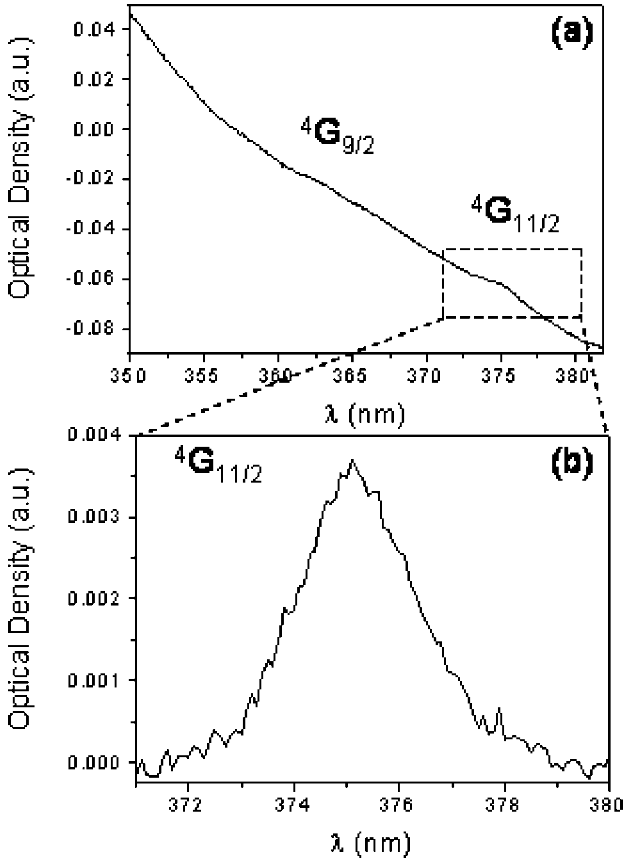

Figure 4. Optical absorption spectrum of a dispersion of Er-doped GaN submicrometer rods on ethanol: (a) general view showing the $^4G_{9/2}$ and $^4G_{11/2}$ absorption bands of Er^{3+} as well as the UV band-edge of GaN, (b) a detailed view of the $^4G_{11/2}$ manifold.

Additional evidence for the incorporation of Er in the GaN submicrometer rods were provided by characterizing these rods by optical absorption and confocal microscopy. Figure 4 shows the optical absorption spectrum of Er-doped GaN rods near the bandgap of the semiconductor. Two small peaks on this spectrum indicate the presence of the $^4G_{9/2}$ and $^4G_{11/2}$ optical absorption manifolds of Er. Because of the low concentration of the dispersion in Er-doped GaN rods, the intensity of the absorption bands recorded is extremely low, which hindered us from resolving the fine structure expected in these bands. However, the position of the manifolds shown in Figure 4, at 362 and 375 nm, lets no doubt about the origin of these bands caused only by Er incorporated in the rods.[20]

Figure 5a shows an image of an Er-doped GaN rod attached to a Ga/N/catalyst alloy particle under excitacion at 488 nm. Both the Er-doped GaN rod and the catalyst cluster containing Er show emission in the 495–540 and

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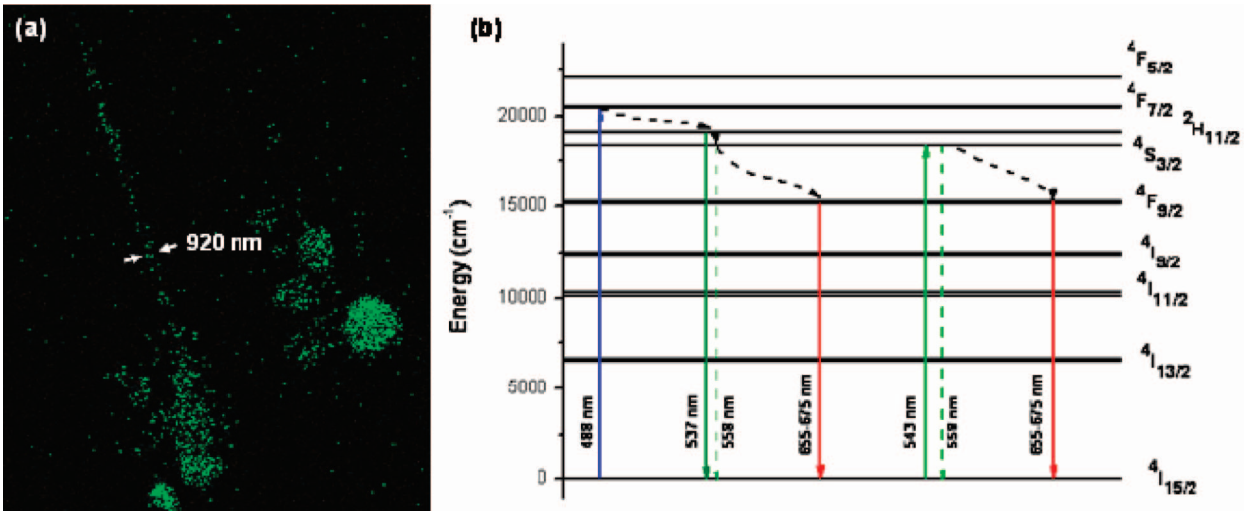

Figure 5. (a) Optical confocal micrograph of a Er-doped GaN submicrometer rod attached to a Ni-based cluster with emission in the 490–540 nm range window of the CCD camera attached to the confocal microscope, after excitation with the 488 nm line of an argon laser. (b) Schematic representation of the energetic levels of Er^{3+} with detailed information of the optical transitions observed in the Er-doped GaN rods.

640–900 nm regions. However, no emission was observed in the 560–610 region. When the Er-doped GaN rods are excited at 543 nm, emission was observed only in the 640–900 nm region. No emission was observed, however, when pumping at 633 nm.

The observation of the emissions coming from these Er-doped GaN submicrometer rods at different regions depending on the excitation energy used can be explained as follows. The electronic structure of Er consists of a partially filled 4f shell, efficiently shielded by the closed and outer $5s^2$ and $5p^6$ shells. This gives rise to sharp absorption and emission lines generated by 4f−4f intraconfigurational transitions, whose position is almost independent of the host material in which the lanthanide ion is embedded because of the weak influence of the ligand environment on the electronic cloud of the Ln ions. These transitions have an electrical dipole origin. They are thus forbidden to first order by the Laporte's parity selection rule, if we consider the ion in its free state. However, when a Ln^{3+} ion is embedded in a host (in our case, Er embedded in a III−V semiconductor), the crystal field generated by the crystalline matrix interacts with the active Ln ion as an external electric field.[21] This means that the crystal field can be understood as a perturbation on the electronic cloud of the central Ln ion caused by the surrounding ions, producing a splitting of the energy levels and a mixing of states of opposite parity, which allow certain of those electric dipole transitions to happen.

Pumping at 488 nm causes the excitation of Er through the absorption of light by the $^4F_{7/2}$ manifold, located at around 490 nm in most of the crystalline materials containing Er^{3+}.[20] From this electronic level, the system can relax nonradiatively to the $^2H_{11/2}$ manifold, from which emission can be produced at 537 nm when the system relaxes radiatively to the ground level ($^4I_{15/2}$).[6] This emission can be detected with the 495–540 nm window of the photomultiplier tube attached to the confocal microscope. The other expected emission in the green coming from Er at 558 nm[5,6] could not be observed, as the detection windows of the photomultiplier tube did not cover this range. The emission detected in the 640–900 nm region is that corresponding to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition, which has been observed in the range between 655 and 675 nm in other matrices.[22] The transitions involved in all these processes are summarized in the schematic diagram of electronic energetic levels of Er in Figure 5b. When exciting at 543 nm, Er is stimulated through absorption of light by the $^4S_{3/2}$ manifold. The fact that emission is observed only in the 640–900 nm region indicates that the system relaxes nonradiatively from this level to the $^4F_{9/2}$ manifold, from which it can emit in the red range through the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. The transitions involved in these processes are also represented in Figure 5b. Emission in the red range has been observed only in GaN when doped with Eu.[23] Finally, the fact that no emission is observed when exciting at 633 nm also constitutes evidence of the presence of Er in these rods, as no absorption bands corresponding to Er can be found at this wavelength. The system cannot be stimulated and no emission can be recorded. Although other emissions corresponding to Er should be expected in the near-infrared (around 1.5 μm), they could not be recorded because of the limitations of our detection system.

The difference in intensity between the emission of the submicrometer rod and the particles that are surrounding it can be attributed to two different origins. If we suppose that the particles that surround the Er-doped GaN rod are rests of the Ni-based clusters from where these rods were originated, then we can consider that the concentration of Er in the rod could be smaller than the concentration of Er in the Ni-based clusters. Another possibility, more interesting, may arise if we consider that the rod acts as an optical waveguide for the green emission of Er, as already reported for blue-emitting GaN nanowires.[10] The emission observed

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from the rod then originated by the optical losses in its lateral walls, having a much lower intensity than the one that we would be able to observe at the end of the rod. In this context, the brilliant particle that can be observed in this picture next to the rod could also be attributed to another rod perpendicularly aligned with respect to the objective of the microscope.

In summary, Er-doped GaN submicrometer rods have been successfully synthesized and some of their spectroscopic properties characterized. It is especially important the observation of green and red emissions coming from Er in these rods obtained by directly pumping Er at energies below the bandgap of the semiconductor at room temperature. We have reported the position of the optical absorption bands corresponding to Er near the band gap of the semiconductor. The identification of these bands might make it possible to enhance the quantum yields of the emissions corresponding to Er by carefully designing the host environment. This engineered environment can be achieved by tailoring the bandgap of the nitride host via an appropriate solid solution in the GaN, InN, and AlN system, to adjust it to fit perfectly with the desired absorption band of Er. This strategy can help to solve the hindering in the application of Er-doped GaN thin films and nanostructured materials because of the poor quantum yield observed at the characteristic wavelengths of the bound-exciton radiation, at around 358 nm, as well as at wavelengths generated by Er in the IR region at around 1.54 μm when stimulated electrically.[24] This approach is not only valid for Er but can also be extended to the rest of the Ln ions embedded in III-nitride semiconductors. Such Ln-doped submicrometer rods have been grown on Si (001) substrates, which may result in the availability of light sources built directly on Si substrates and operating at wavelengths throughout the visible and near-infrared range without any other postgrowth process. The integration of electronics and photonics on a single Si substrate may result in the development of on-chip optoelectronics incorporated with electronic circuits and optical devices. In the future, through codoping with multiple Ln ions, the emission spectrum can be further customized and the perceived color varied over a very wide range. This is further evidence of the versatility of the incorporation of lanthanide ions in the III-nitrides approach to light emission that is not feasible with semiconductor alloys alone.

In our opinion, the results presented in this letter open new avenues for designing novel optoelectronic devices based on lanthanide-doped III-nitride one-dimensional submicrometer and nanostructures. Such Ln-doped GaN one-dimensional structures may be used to fabricate cost-efficient, full-color displays, as was suggested for Er-doped GaN powders,[6] dispersing the nanostructures into the appropriate polymers to disaggregate them. The advantage of using Er-doped GaN one-dimensional structures is the possibility of controlling their growth direction, taking advantage of the anisotropic properties of GaN to fabricate these full color displays, with implications in the polarization of the emitted light.

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