Doped gallium oxide nanowires for photonics

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ABSTRACT

Monoclinic gallium oxide, β-Ga_2O_3, is a transparent conducting oxide (TCO) that presents one of the widest band gaps among this family of materials. Its characteristics make it highly interesting for applications in UV – visible - IR optoelectronic and photonic devices. On the other hand, the morphology of nanowires made of this oxide presents specific advantages for light emitting nanodevices, waveguides and gas sensors. Control of doping of the nanostructures is of the utmost importance in order to tailor the behavior of these devices.

In this work, the growth of the nanowires is based on the vapor-solid (VS) mechanism during thermal annealing treatment while the doping process was carried out in three different ways. In one of the cases, doping was obtained during the growth of the wires. A second method was based on thermal diffusion of the dopants after the growth of undoped nanowires, while the third method used ion implantation to introduce optically active ions into previously grown nanowires. The study of the influence of the different dopants on the luminescence properties of gallium oxide nanowires is presented. In particular, transition metals and rare earths such as Cr, Gd, Er or Eu were used as optically active dopants that allowed selection of the luminescence wavelength, spanning from the UV to the IR ranges. The benefits and drawbacks of the three different doping methods are analyzed. The waveguiding behavior of the doped nanowires has been studied by room temperature micro-photoluminescence.

KEYWORDS: Gallium oxide, nanowire, waveguide, optically active ions, chromium, rare earth ions, europium, gadolinium

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1. INTRODUCTION

The study of monoclinic gallium oxide, β-Ga_2O_3, has raised a strong interest during the last decades due to the potential applications of this material [1-5]. Most of these applications emerge from the fact that this oxide presents n-type electronic properties [1, 4], which are under study in order to gain control on them [4], with clear applications, such as gas sensors [6]. This conduction properties are present in spite of the fact that β-Ga_2O_3 has one of the widest band gaps (around 4.9 eV) among the transparent conductive oxides (TCOs) family, making it transparent down to about 260 nm [7]. Besides, its refractive index is fairly high [8] in the IR - visible – UV range (1.8 – 2.1), which is of interest for photonics in this range, mainly in the UV range. These properties make the optoelectronics and, in general, photonics applications as one of the areas for which this material is most interesting.

Furthermore, the growth of low dimensional structures, and in particular semiconductor nanowires [9], provides useful advantages for photonics applications, such as waveguides or very local and well oriented emitting devices [10, 11]. In this work, we present our results on the control of optical properties of gallium oxide nanowires doped with optically active ions, particularly, chromium and some rare earth ions like gadolinium, europium and erbium. Their characteristic intraionic emission lines range from UV (315 nm) to IR (1545 nm). Luminescence properties with high spatial resolution have been studied by means of cathodoluminescence (CL) in the scanning electron microscope (SEM). Waveguiding behavior of both excited and transmitted light through the structures was also studied by room temperature micro-photoluminescence.

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2. EXPERIMENTAL

Undoped gallium oxide nanostructures have been obtained as reference samples by a vapor-solid growth mechanism from metallic gallium in a tube furnace, as explained elsewhere [12]. The substrate was a gallium oxide pellet and no catalyst was used. In order to dope the structures, three different methods were used. The first one was based in doping during the growth process itself, by placing powders of the oxide of the dopant ion (europium or erbium) to form a mixture with gallium oxide powder. A thermal treatment in two steps was performed: a first one at 1500 ºC and a second one at 1350 ºC, as explained in Refs. [12, 13]. The second doping method, used for chromium doping, was based on diffusion of the dopant into previously grown, undoped gallium oxide nanostructures. The diffusion process was carried out at 1500 ºC. The third method is based on ion implantation [14]. Undoped gallium oxide nanostructures were placed on a silicon substrate and ion implantation was performed either with europium or gadolinium ions with an energy of 150 keV and a fluence of $5x10^{15}$ cm^{-2}. In order to obtain crystal recovery after implantation, thermal annealing of the implanted samples has been performed at temperatures in the range 500 ºC - 1100 ºC in an inert gas atmosphere.

Morphological characterization was carried out in a Leica Stereoscan 440 or a FEI Inspect S50 scanning electron microscope (SEM). Cathodoluminescence (CL) measurements have been performed within the above mentioned Leica system or a Hitachi S2500 SEM. CL spectra were recorded with a Hamamatsu PMA-11 charge coupling device camera. For Raman analysis, a Horiba Jobin Yvon LabRam HR 800 confocal microscope was used, with an excitation wavelength of 325 nm given by a HeCd laser. For micro-photoluminescence (μ-PL) analysis, an optical microscope was used. In this case, the 366 nm (3.39 eV) or 436 nm (2.84 eV) emission lines of a Hg lamp illuminated the structures in order to excite their luminescence.

3. RESULTS AND DISCUSSION

Figure 1 shows SEM images of different structures which have been doped with Er, Eu, Gd or Cr. Figures 1(a) and (b) show representative nanostructures obtained by the mixture method and doped with Er and Eu, respectively. Figure 1 (c) corresponds to Gd implanted nanowires, with sizes in the range of a few hundred nanometers, which is representative of the morphology of both the Eu and Gd implanted nanostructures, typically longer and thinner than those obtained by the powder mixture method. Finally, figure 1(d) shows the secondary electrons image of a chromium doped nanostructure by impurity diffusion. As a general feature, a high density of long nanowires is obtained when metallic gallium is used as precursor and ordered shorter needles are obtained in the case of the powder oxides mixture method. On the other hand, growth in a preferential direction is obtained for the latter samples.

EDX microanalysis measurements confirm the incorporation of dopant impurities into the nanostructures. Figure 2(a) shows EDX spectra from individual nanowires placed on a Si substrate and doped either with Eu or with Gd by ion implantation. The spectra confirm that the ions have been introduced within the structures effectively in both cases. Simulations for the implantation conditions indicate that the penetration of the ions is in the range of some tens of nanometers. Furthermore, these spectra were acquired after thermal annealing was carried out, which is needed in order to recover crystal quality after the serious damage that is created by ion implantation. This result shows that there is no significant out-diffusion of the implanted ions during the annealing treatment, which could result in a limitation for this doping method. The observed Si peak comes from the substrate.

The EDX spectrum from a Cr^{3+} doped nanowire placed on a Si substrate is shown in figure 2(b). The inset shows a detail of the peak corresponding to chromium, thus confirming the effective doping of the wires by using the diffusion doping method. The very intense Si peak observed in this spectrum comes from the substrate.

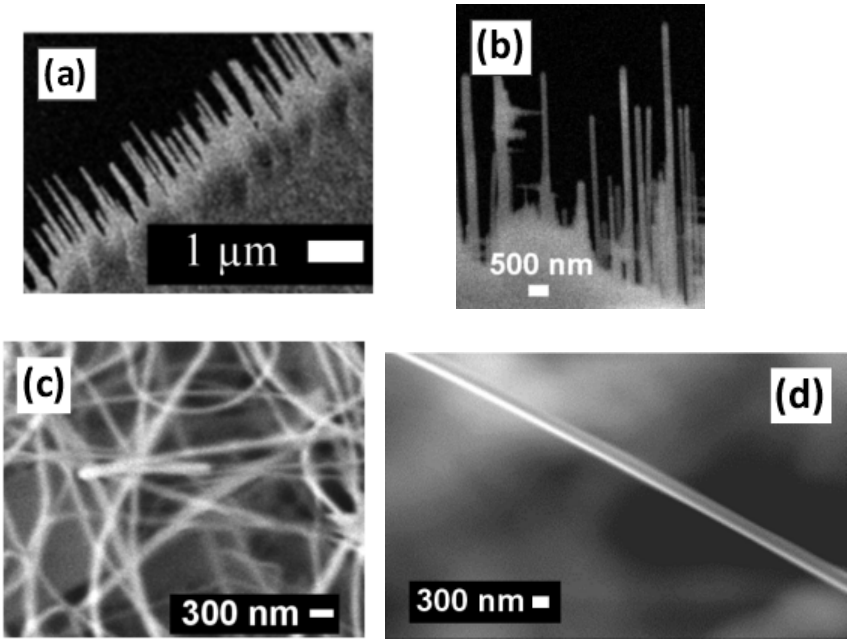

Figure 1. SEM images of representative structures for the (a) Er doped sample by the powder mixture method, (b) Eu doped sample by the powder mixture method, (c) Gd doped sample by the ion implantation method and (d) Cr doped sample by the diffusion method.

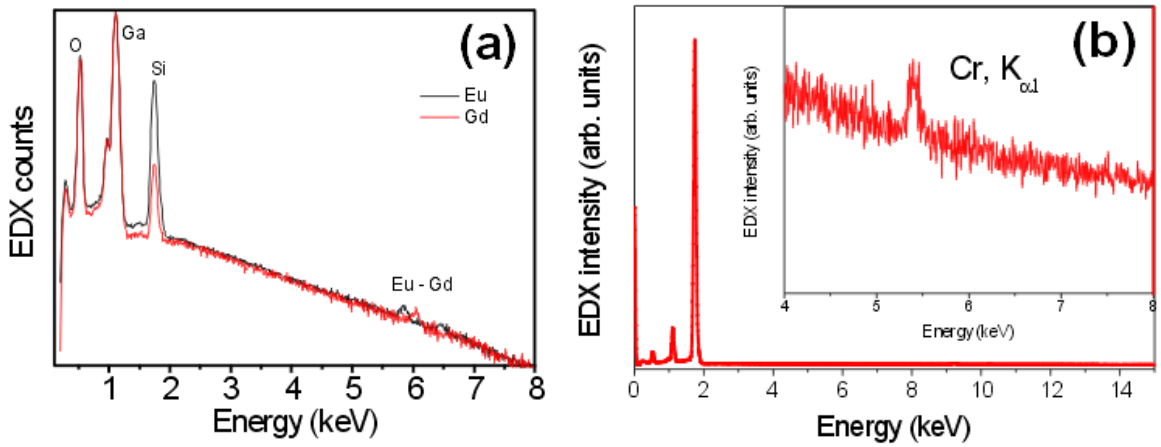

Figure 2. EDX spectra from (a) Eu or Gd ion implanted nanowires after thermal annealing and (b) chromium doped nanowires.

The crystal quality of doped nanostructures has been investigated by Raman spectroscopy. Figures 3(a) and (b) show the optical image and the Raman spectrum of an individual nanowire with a thickness of several hundred nanometers, placed on a silicon substrate, implanted with Eu and subsequently annealed at 900 ºC. This spectrum is representative of the results obtained for the doped samples and shows Raman peaks at 200, 346, 416, 475, 627, 657 and 765 cm^{-1}, all of them associated to monoclinic gallium oxide, β-Ga_2O_3 (see figure 3(d) for comparison with an undoped nanowire). It is also indicated in the figure that a very strong peak appearing in 520 cm^{-1} is due to the silicon substrate. Therefore, thermal annealing after implantation is shown to effectively remove the implantation damage and recover a good crystal quality,

which is necessary for an optimum optical activation of the luminescent ions. Similar results are obtained for the Gd implanted sample.

Figure 3(c) shows the Raman spectrum of a Cr^{3+} doped nanostructure, presenting the same peaks and confirming that the crystal structure again corresponds to β-Ga_2O_3. The presence of chromium ions does not affect the peaks positions or widths. Finally, figure 3(d) shows the spectrum of an undoped nanowire, for comparison.

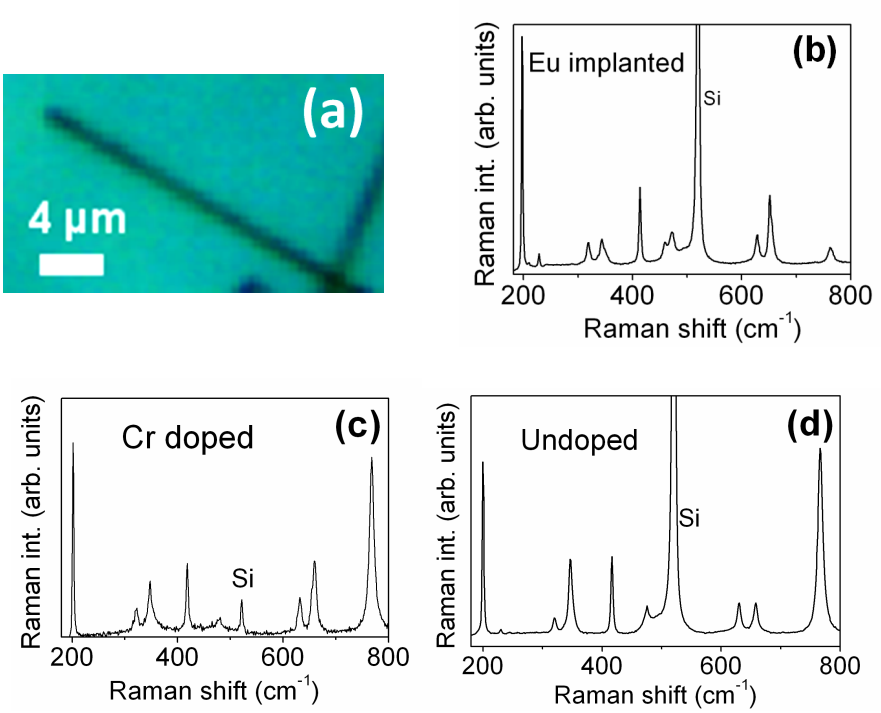

Figure 3. (a) Bright field optical image and (b) Raman spectrum from an Eu implanted nanowire. It was thermally annealed at 900ºC after ion implantation. The strong peak at 520 cm^{-1} corresponds to the monocrystalline silicon substrate, while the rest of the peaks correspond to β-Ga_2O_3. (c) Raman spectrum from a Cr^{3+} doped nanowire. (d) Raman spectrum of an undoped nanowire.

We have studied the luminescence bands due to the presence of optically active impurities by CL and PL. Figure 4 shows the room temperature CL spectra for the different gallium oxide samples in the range of interest. The characteristic peaks corresponding to Eu^{3+} (red, around 610 nm), Cr^{3+} (red, peaked at around 720 nm), Gd^{3+} (UV, around 315 nm) and Er^{3+} (green, around 550 nm, and IR, around 1445 nm) optically active ions are shown. Besides, the characteristic β-Ga_2O_3 UV-blue band associated with typical defects, either intrinsic [1] or impurities [3], is also plotted. This band has been often observed in luminescence studies of gallium oxide and is usually very intense. It is also considered as one of the bases for full-range luminescent devices based on this oxide [15]. Therefore, with the proper selection of these optically active ions, it is possible to cover, not only the visible range (Er^{3+}, Eu^{3+} and Cr^{3+}), but also well into the UV and IR ranges, making the best of the optical transparency of monoclinic gallium oxide.

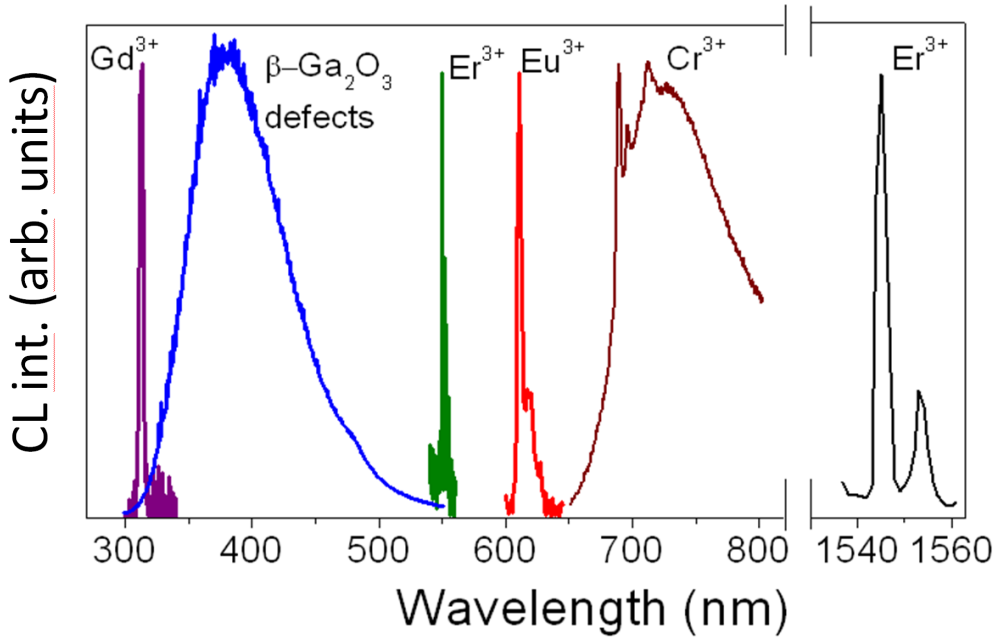

Figure 4. Room temperature CL spectra from the structures doped with the different optically active ions, showing the peaks that cover the UV-visible-IR range. Besides, the defect band associated to nominally undoped monoclinic gallium oxide is shown in the violet-blue region.

Figure 5 shows several examples of gallium oxide structures doped with optically active ions. All of them exhibit waveguiding behavior. Figures 5(a) and (b) show the bright field and the room temperature micro-PL images, respectively, of a chromium doped nanowire with about 600 nm width and several tens of microns length, as observed in figure 5(a). The excitation wavelength was the 436 nm line of a Hg lamp and illumination of the wire was homogeneous. The micro-PL image shows red emission from the nanowire, due to both the R lines (^2E – $^4A_2$ transition) and the $^4T_2$ – $^4A_2$ phonon-assisted broad band [16] of the Cr^{3+} (spectrum shown in figure 4, centered on about 720 nm). The right end of the nanowire shows, in figure 5(b), a bright red spot characteristic for waveguiding behavior. A much weaker red emission is observed along the wire, which means that certain losses were occurring but that most of the light was being guided. It is worth noticing that the wire dimensions are a bit smaller than the wavelength (around 700 nm) for this specific Cr^{3+} emission. The behavior is similar to that observed in straight, Cr^{3+} doped nanowires [11] with the same or bigger dimensions.

Figures 5(c) and (d) show the bright field and room temperature micro-PL images of an Eu^{3+} doped needle with a size in the range of microns. Excitation wavelength for the micro-PL image was the 366 nm line of a Hg lamp. This sample was doped by the powder mixture method. The red emission is due to the intraionic luminescence lines of the europium ion, whose most intense line is at around 610 nm due to the $^5D_0$ – $^7F_2$ transition [12]. For these structures, evidence that some luminescence could be due to $Eu_3Ga_5O_{12}$ garnet were found [12] and it is not ruled out that the luminescence observed in this image could be due both to Ga_2O_3:Eu and the europium ions that form part of the garnet crystal structure. This needle presents waveguiding behavior and losses which could be assigned to the presence of defects within the nanowires and/or roughness of the surface. The waveguiding effect was reported for similarly obtained Eu doped structures in a previous work [12]. In that case, the effect was observed also for planar structures.

Figures 5(e) and 5(f) show the bright field and the room temperature micro-PL image of a nanowire doped with Er by the powder mixture method. Excitation wavelength for the image was the 366 nm line of the Hg lamp. Its width is in the range of several hundred nanometers and its length is around 35 μm. The contrast in figure 5(e) is very low, which is explained by the fact that the substrate and the nanowire are both β-Ga_2O_3 and the strong contrast observed for the

substrate surface, due to its roughness. On the other hand, the micro-PL image shows very clearly a luminescence intensity enhancement from the nanowire and, even stronger, from the wire ends, confirming the waveguide effect. Green emission was already observed in Er doped gallium oxide nanowires behaving as lightguides [11]. As in the case of the Eu doped structures obtained by the powder mixture method, formation of the $Er_3Ga_5O_{12}$ garnet was observed in this wires, which influences in their light emission spectrum [11, 17].

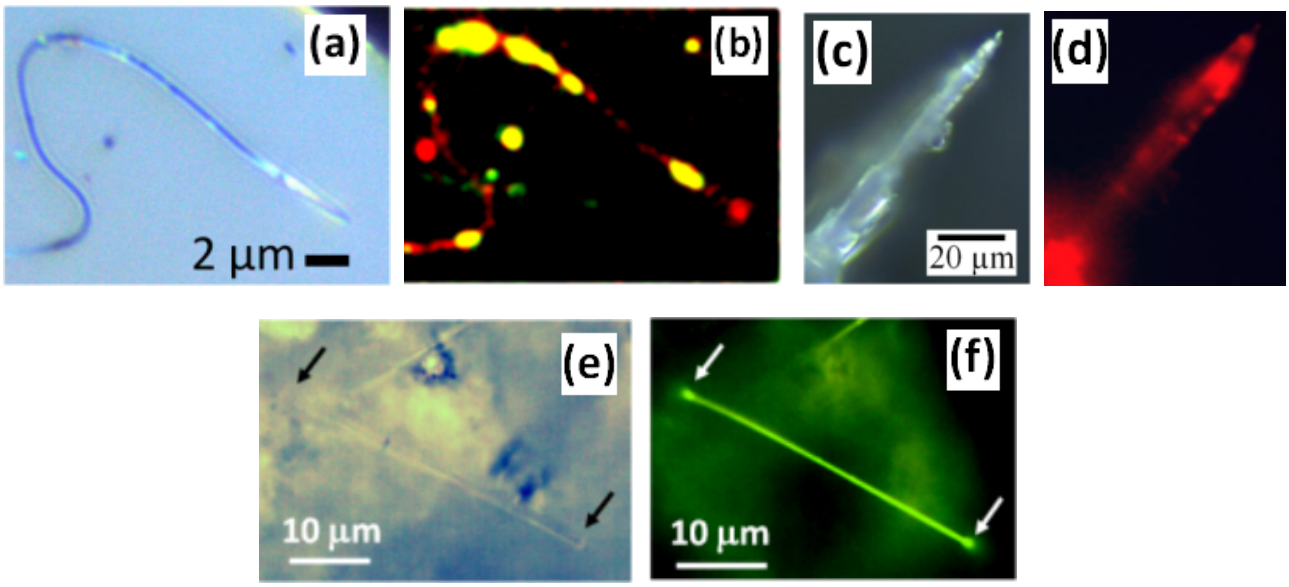

Figure 5. (a) Bright field optical image and (b) room temperature micro-PL image of a Cr^{3+} doped nanowire, λ_{exc} = 436 nm. (c) Bright field optical image and (d) room temperature micro-PL image of a Eu^{3+} doped microneedle, λ_{exc} = 366 nm. (e) bright-field optical image and (f) micro-PL image of an Er^{3+} doped nanowire, λ_{exc} = 366 nm.

4. CONCLUSIONS

Elongated nanostructures based on monoclinic gallium oxide have been doped with several optically active ions, such as Cr^{3+}, Er^{3+}, Eu^{3+} or Gd^{3+}. Growth and doping of the nanowires was achieved through different methods. All of them resulted in an effective inclusion of the mentioned ions into the gallium oxide lattice as dopants, as well as their optical activation. Therefore, we have achieved wavelength-controlled luminescence from the nanowires in the UV – visible – IR range. Doping by thermal annealing of a powder mixture (gallium oxide + rare earth oxide) resulted in ordered arrays of nanowires. However, the distribution of the ions was not completely homogeneous and formation of a certain amount of $RE_3Ga_5O_{12}$ garnet during growth was observed. Diffusion was successfully used in order to dope the nanostructures with Cr^{3+}, to an amount of about 1 at. %. The main drawback of this method is the lack of a high control on the dopant concentration, which is more critical for the rare earths. Finally, we also carried out ion implantation into undoped nanowires. Luminescence was observed, even before annealing, for Eu^{3+} doped wires. For Er^{3+} and Gd^{3+} ions, subsequent annealing was needed in order to get intense rare earth luminescence. Waveguiding behavior has been shown for the nanowires: they behave at the same time as light emitters and guides.

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