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Raman and cathodoluminescence analysis of transition metal ion implanted Ga_2O_3 nanowires

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ABSTRACT

The structural and luminescence properties of gallium oxide nanowires doped with chromium or manganese have been investigated. Undoped Ga_2O_3 nanostructures have been fabricated by a thermal evaporation method, while doping was subsequently achieved by ion implantation followed by thermal annealing. Scanning electron microscopy (SEM) analysis has shown that this doping process does not alter the morphology of the nanostructures. Ion implantation results in partial amorphization of the crystal lattice, as deduced from Raman spectroscopy studies. Thermal annealing at different temperatures was carried out in order to restore the crystallinity of the nanowires. Raman spectroscopy analysis demonstrates that recrystallization starts at about 700 °C and a complete recrystallization is achieved at about 1000 °C. Cathodoluminescence (CL) analysis has been used to study the emissions in the 300–900 nm range. As-implanted nanowires virtually do not emit any light, which is related to their poor crystal quality and the implantation induced defects. Thermal annealing results in effective CL emission. In particular, a clear correlation between crystallinity of the nanowires doped with Cr and the emission from the ^2E-$^4A_2$ and $^4T_2$-$^4A_2$ intraionic transitions has been observed. On the other hand, emissions directly related to intraionic transitions of Mn have not been found in the nanowires implanted with this ion. The influence of the implantation process and annealing temperature on the observed changes in the donor-acceptor pairs (DAP) band of Ga_2O_3 is discussed.

1. Introduction

During the last years, a large number of works on nanowires and other nanostructures based on semiconductor materials have been reported [1,2]. Particularly, the study of the transparent conductive oxides (TCO) nanomaterials is of applied interest as these materials can be used as active part in optoelectronic nanodevices, due to their electrical conductivity and wide transparency in the ultraviolet (UV)–visible range [3]. Both their electrical and optical properties can be tailored by suitable doping, allowing control on both the carrier density and the luminescence bands [4,5]. On the other hand optically active ions, such as rare earths and transition metals, are often used as dopants for high efficiency luminescence emission. Besides, TCOs usually present characteristic luminescence bands the origin of which is normally related to native defects such as oxygen vacancies [6]. Monoclinic gallium oxide (β-Ga_2O_3) presents one of the widest band gaps ($E_g \approx$ 4,9 eV) among the TCOs, which results in a very wide transparency range, from the infrared (IR) to the ultraviolet (UV, about 260 nm). This makes β-Ga_2O_3 nanostructures doped with appropriate optically active ions very interesting, with potential applications in a wide spectral range in optoelectronics [7,8]. Undoped Ga_2O_3 usually exhibits ultraviolet-blue luminescence coming from the native defects [9,10], while Cr doping of Ga_2O_3 leads to an intense red emission, which becomes the dominant one in the case of nanowires when compares with bulk material [11,12]. There are several methods to dope the nanostructures [13]. One of them is thermal diffusion of the desired impurity by means of thermal treatments. This process may not be effective if the structure presents very high crystal quality, as it makes it difficult to introduce dopant atoms, or if the dopant presents a very low solubility. Another option is ion implantation [14,15], which allows a very efficient control of the dopant concentration and the penetration depth of the ions within the sample. In order to optimize the optical emission of the implanted ions, the crystal damage

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induced by the ion implantation must be removed. Then thermal annealing is required after the implantation process to restore the crystal lattice. We have previously reported rare-earth doping (Er, Eu, Gd) of Ga_2O_3 nanowires by ion implantation [16]. Obtention of luminescence in nanowires after ion implantation also requires crystal recovery treatments, which result in a change of the defects structure. This would affect the luminescence properties of the nanostructures. Therefore, understanding the lattice recovery correlation with the luminescence is of utmost importance.

In this work, β-Ga_2O_3 nanowires have been doped by ion implantation with chromium and manganese ions in order to study the luminescence emission at room temperature. In order to get a better understanding of the luminescence properties, bulk β-Ga_2O_3 crystals have also been implanted with the same ions and under the same conditions. Samples from both sets, bulk and nanostructured, have been annealed at different temperatures. Raman spectroscopy has been used to analyze the crystal quality and CL was used to study the luminescence properties of the samples. Correlation between both properties will be discussed.

2. Experimental

Undoped β-Ga_2O_3 nanostructures were grown by a thermal evaporation method based on the vapor-solid (VS) growth mechanism, avoiding the use of a catalyst. A pellet with 2–3 mm thickness formed by Ga_2O_3 compact powders was used as a substrate on which a piece of metallic gallium was placed. The thermal treatment was conducted in an open furnace that enables the oxidation of the metallic Ga, at 1150 °C for 8 h under an Ar flux of 0.8 l/min. This resulted in the growth of a great amount of micro- and nanostructures. After this treatment, many of these structures were deposited on Si substrates for ion implantation. On the other hand, β-Ga_2O_3 bulk single crystals were grown using the floating zone technique in a set-up equipped with two halogen lamps and the corresponding ellipsoidal mirrors. Growth details have been reported previously [17]. The crystals were cleaved on the (1 0 0) plane, and subsequently cut into $\sim 5 \times 5$ mm^2 samples. Sets of each kind of samples were implanted with chromium and manganese. The implantation conditions were 150 keV energy and a fluence of 10^{15} cm^{-2} for both kinds of ions. Rapid thermal annealing (RTA) treatments at 700 °C, 900 °C or 1100 °C were performed in both bulk and nanostructured samples, in order to repair the crystal damage induced by ion implantation. Another set of samples remained as-implanted. Therefore, sixteen samples have been studied: bulk Ga_2O_3:Cr, bulk Ga_2O_3:Mn, Ga_2O_3:Cr NWs, Ga_2O_3:Mn NWs, each of them as-implanted or annealed at 700, 900 or 1100 °C, as it is shown in Table 1. The morphology of the nanostructures was assessed by a Leica Stereoscan 440 scanning electron microscope (SEM). Crystal structure was analyzed by micro-Raman spectroscopy, using the 325 nm line of a HeCd laser as excitation line in a Horiba Jobin Yvon LabRam HR800 confocal microscope. Luminescence studies were carried out using the CL technique in a Hitachi S2500 SEM.

Table 1
Summary of the samples.

	Cr implanted	**Mn implanted**
Ga_2O_3 nanowires	As-implanted	As-implanted
	700 °C	700 °C
	900 °C	900 °C
	1100 °C	1100 °C
Bulk Ga_2O_3	As-implanted	As-implanted
	700 °C	700 °C
	900 °C	900 °C
	1100 °C	1100 °C

3. Results and discussion

Fig. 1 shows a SEM image of a sample with nanowires implanted with Mn and annealed at 700 °C, which is representative of the doped β-Ga_2O_3 nanowires after ion implantation and subsequent thermal annealing. Most of the structures are elongated, such as nanowires, nanobelts or nanoribbons, with lateral dimensions ranging from hundreds of nanometers to several microns, and lengths that can reach several hundred microns. Their thicknesses can be between tens and hundreds of nanometers. No significant aspect ratio variations have been observed between the different samples. These morphologies are similar to those previously found for β-Ga_2O_3 nanowires and nanoribbons, either ion implanted [15], doped by thermal diffusion [18] or undoped [19], showing that the nanowire morphology is retained after the doping by ion implantation.

In order to analyze the crystal structure after the RTA treatments, local micro-Raman analysis has been performed on individual nanostructures from each sample. Fig. 2(a) shows spectra acquired from Cr doped nanowires. A clear evolution of the Raman spectra when raising the annealing temperature can be observed. Raman spectra from undoped β-Ga_2O_3 with good crystal quality present a set of ten peaks centered at 167, 200, 320, 346, 416, 475, 627, 651, 657 and 765 cm^{-1} [18,20]. It is well known that Raman peaks broaden when there is disorder in the material or it presents crystal damages [21]. As-implanted nanowires do not present any Raman peaks, indicating a very low crystal quality. Due to their very low thickness, the whole nanostructures have been completely amorphized [14].

In the Raman spectra from the 700 °C annealed nanowires, defined peaks start to be observed, but with a full width at half maximum (FWHM) wider than for those structures annealed at higher temperatures. This broadening of the FWHM for the lower annealing temperature is due to an incomplete recovery of the implantation damage. On the other hand, at 900 °C and 1100 °C the crystal structure seems to be completely recovered. It was previously observed [14] that β-Ga_2O_3 nanostructures implanted with rare earths in similar conditions started to recover their crystallinity in the 500–700 °C range and complete recovery was reached between 900 °C and 1100 °C, in good agreement with the results reported in the present work. The results obtained from the Mn implanted nanostructures (Fig. 2(b)) are similar. The atomic weights of Cr and Mn are very close and therefore, a similar implantation damage is expected in the two cases, what allows deducing that crystal recovery should evolve with the annealing temperature in the same way. This is observed in Fig. 2. In fact, the annealing temperature necessary for a complete crystal recovery was estimated for β-Ga_2O_3 to be around 1100 °C [14] in agreement with the results shown here.

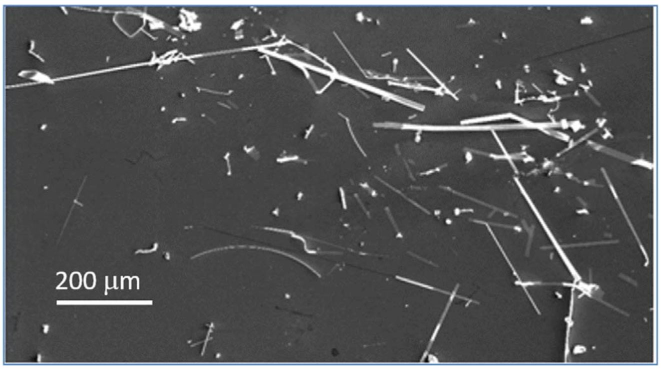

Fig. 1. SEM image showing β-Ga_2O_3 nanowires doped with Mn and annealed at 700 °C.

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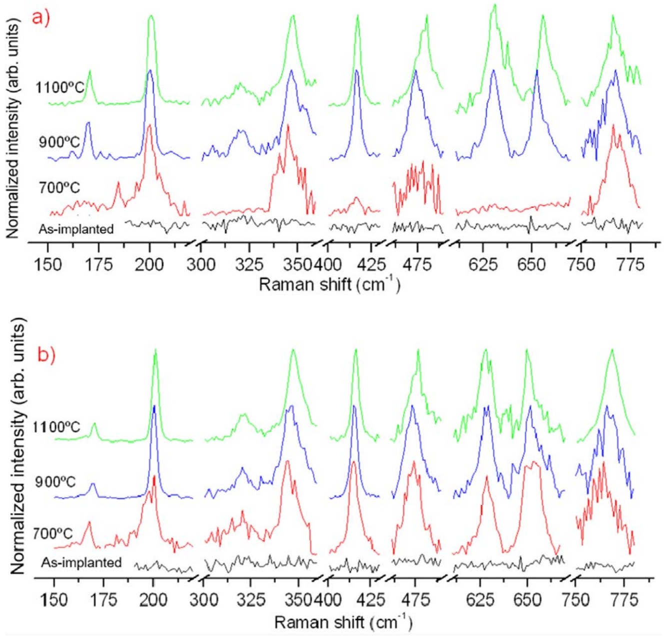

Fig. 2. Raman spectra from (a) Cr β-Ga_2O_3 nanowires, as implanted (lower spectrum) or annealed at 700 °C, 900 °C or 1100 °C (upper spectrum) (b) Mn implanted β-Ga_2O_3 nanowires. Intensities are normalized and vertically shifted for the sake of clarity.

Luminescence studies on these samples have been performed by CL spectroscopy at room temperature. The electron beam in SEM was defocused for these measurements in order to keep a lower excitation density, so that the intensity of chromium and manganese intraionic transitions were maximized with respect to the characteristic UV-blue band of gallium oxide. Intraionic transitions of these transition metals present typically long lifetimes [12]. We have used an acceleration voltage of 5 kV so that the penetration depth of electrons is similar to that of the implanted ions [15]. Fig. 3(a)-(b) shows CL spectra from nanowires doped with chromium. As-implanted nanowires show a very low emission intensity, although a weak broad band in the 700–900 nm region can be appreciated. In the other three spectra, corresponding to annealed samples, a more intense and narrower red emission band is registered.

Emission bands and lines of Cr^{3+} ions located in different host are well known [22–24]. Particularly, β-Ga_2O_3 nanowires [8,12] emit at room temperature a red-IR luminescence composed by the R lines, due to the ^2E-$^4A_2$ transition at around 690 nm, and a phonon assisted broad band due to the $^4T_2$-$^4A_2$ transition, centered around 730 nm. Relative intensity of the R lines with respect to the broad $^4T_2$-$^4A_2$ band depends largely on the crystal field strength [22], which is directly related to the crystalline environment. The weak red band in the as-implanted sample is assigned to the $^4T_2$-$^4A_2$ band, although it is much broader than in the other three samples, which is explained by the strongly distorted crystal environment. In the sample annealed at 700 °C the $^4T_2$-$^4A_2$ band is not so wide, but the R lines are not observed, indicating that the immediate surrounding of the ions is still quite distorted at this annealing temperature. At 900 °C annealing temperature, the relative intensity of the R-lines is higher, showing the expected emission spectrum for Cr^{3+} ion in β-Ga_2O_3. In the sample annealed at 1100 °C, a similar shape of the emission band is obtained, indicating that at 900 °C crystal recovery was practically complete. These spectra show that the lattice arrangement after annealing gives the Cr^{3+} ions an adequate environment to be efficiently activated. Sharpening of the band and the peaks shows a better crystalline quality, due to a more homogeneous symmetry of the luminescence centers. Therefore, the information obtained from this CL analysis is in agreement with that inferred from the Raman spectra shown in Fig. 2(a). Hence, from these results we can deduce that both sharpening of the band and the presence of the R lines in luminescence spectra could be used as a proof of crystalline recovery of the nanostructures during thermal annealing performed after ion implantation.

On the other hand, the complex donor acceptor pairs (DAP) characteristic luminescence band of β-Ga_2O_3 in the UV-blue region is also observed. This band is quite weaker than the Cr^{3+} emission in all the spectra and, in fact, its relative intensity reduces when the annealing temperature is increased. The complex UV-blue band is shown in more detail in Fig. 3(b). The band appears broadened with respect to the characteristic DAP band observed by CL from undoped β-Ga_2O_3 nanowires [18], and presents an additional component at longer wavelengths, around 460 nm.

Doping of β-Ga_2O_3 nanowires with Mn has been previously studied due to the potentially interesting magnetic properties and luminescence [25]. In a previous work, β-Ga_2O_3 nanostructures with good crystallinity were Mn doped during their growth. They showed an intense emission band centered at 590 nm, as well as a blue-green band centered at 480 nm, depending on the nanostructures morphology [18]. Fig. 3(c) shows CL spectra corresponding to the Mn implanted nanostructures. As-implanted sample presents a very weak emission, as in the case of the Cr implantation. After annealing at 700 °C, a broad band in the blue region, composed by at least two bands with maxima around 360 nm and 450 nm, is observed. In fact, this result is similar to that shown in Fig. 3(b) for the Cr implanted sample. The band in 360 nm is the characteristic defects related band of gallium oxide. The fact of the appearance of the 450 nm band in both Cr and Mn implanted NWs indicates that its origin could be related to the implantation damage. When the annealing temperature is increased to 900 or 1100 °C, a variation of the relative intensity of the two bands (360 and 450 nm) is observed and the former band becomes more intense with respect to the latter. This shows that by controlling the annealing temperature, the luminescence main wavelength from the nanostructures could also be tailored.

The 450 nm band cannot be assigned to intraionic transitions of Mn or even to the presence of Mn itself [18], as it is similar to the band observed in the Cr implanted samples. Besides, the maximum relative intensity of this 450 nm band is seen for 700 °C annealing temperature, what indicates that it can be assigned to defects created during ion implantation, which have not been completely removed after RTA.

CL spectra on the implanted bulk samples series have also been performed. Fig. 4(a) shows spectra corresponding to β-Ga_2O_3:Cr after different annealing temperatures. The spectrum from the as-implanted sample shows the DAP band (around 360 nm) and the characteristic Cr band in the red region. The latter is quite broadened, similarly to the case of the nanostructured sample (Fig. 3(a)). After annealing at 700 °C, the defect band presents a stronger relative intensity than the Cr band. Besides, the latter band does not show the R lines, similar to what was observed in the nanostructured sample. For 900 °C annealing temperature, the Cr band - sharper and showing the R lines – dominates over the UV-blue band. Finally, after annealing at 1100 °C, the UV-blue band is more intense than the Cr-related band. The intensity reduction of the Cr-related luminescence band after 1100 °C annealing may be related to out-diffusion of Cr as it has been observed for Eu-implanted bulk crystals [16]. The red region of the spectrum is zoomed in the inset of Fig. 4(a) for 1100 °C, showing the similarity with the red band for the 900 °C sample.

The identical behavior of the Cr emission in the nanostructures and the bulk samples indicates that the emission centers are the same and that thermal annealing results in a similar effect for both

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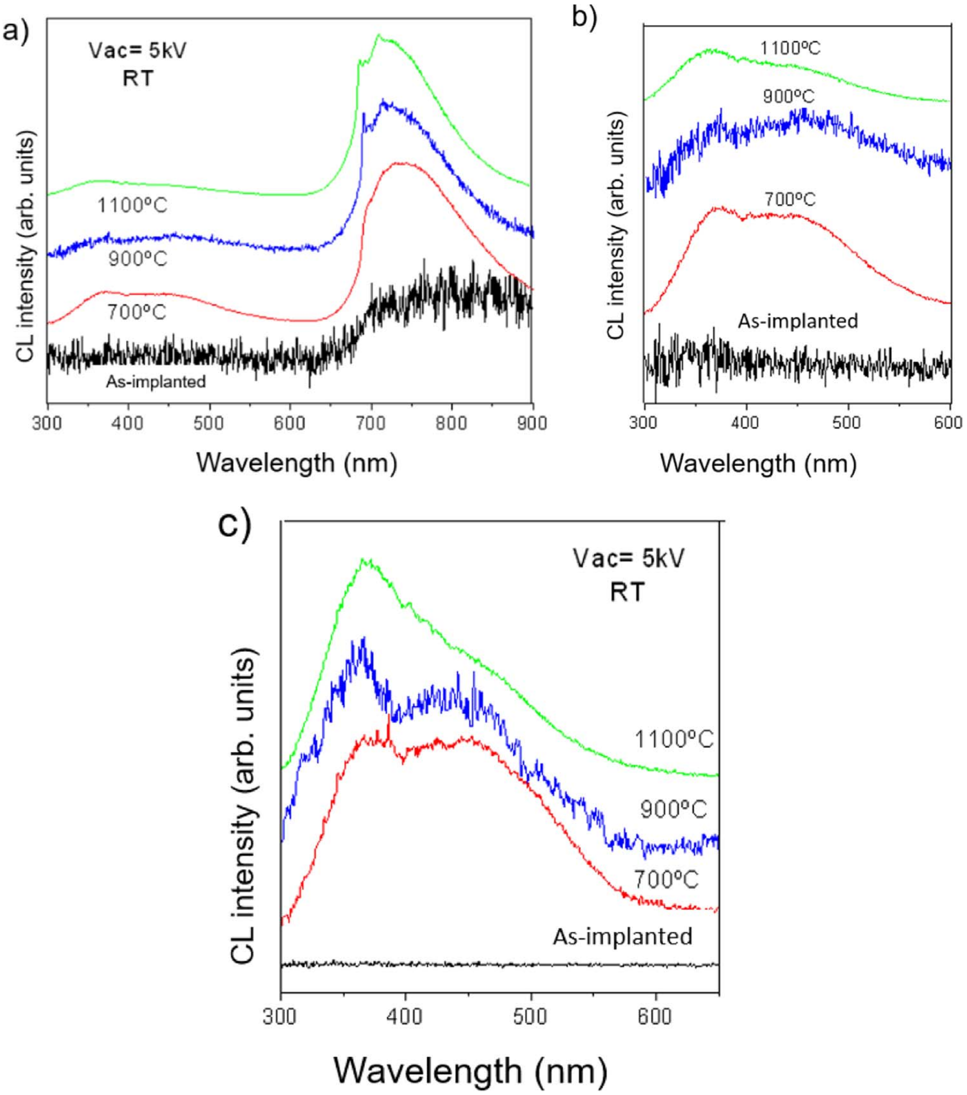

Fig. 3. (a) Normalized room temperature CL spectra from Cr doped β-Ga_2O_3 nanowires. (b) Detail of the 300–600 nm range from the spectra shown in (a). (c) CL spectra from Mn doped β-Ga_2O_3 nanostructures.

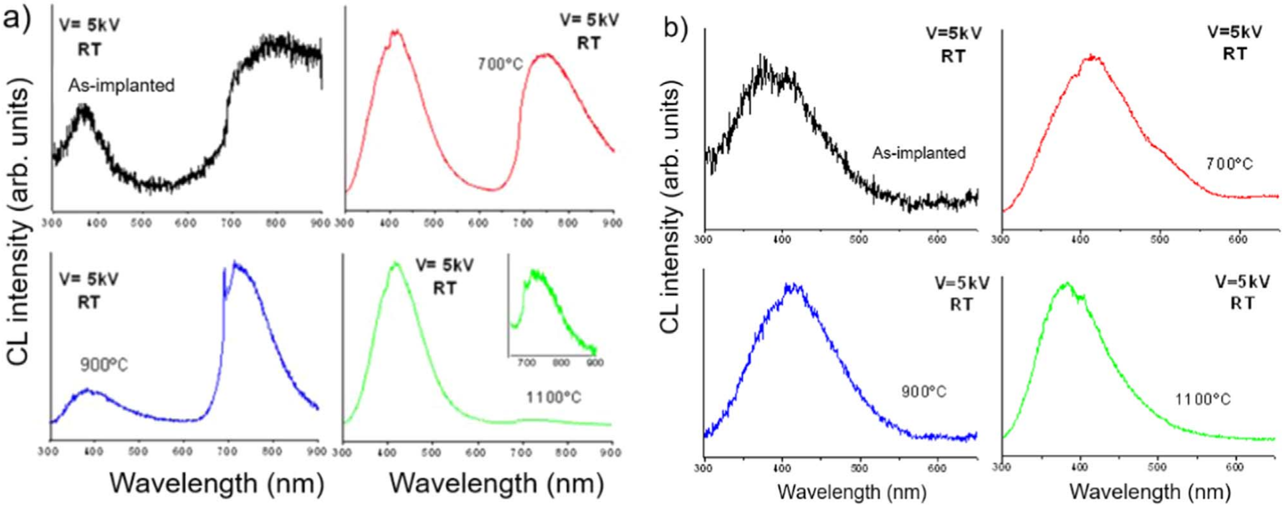

Fig. 4. Normalized room temperature CL spectra from (a) Cr implanted bulk β-Ga_2O_3. (b) Mn implanted bulk β-Ga_2O_3.

kinds of host. On the other hand, there are clear differences between the UV-blue band in the nanowires and the bulk material, which could be related to the different recrystallization process, which takes place in both kinds of samples. This could be tentatively explained by the presence of a crystalline phase below the implanted region in the bulk sample, in contrast to the situation in

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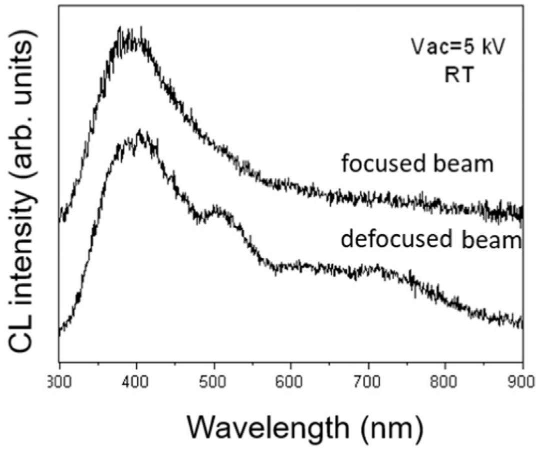

Fig. 5. Room temperature CL spectra acquired at different excitation densities from bulk, Mn implanted β-Ga_2O_3 after 700 °C thermal annealing. The intensity has been normalized and spectra have been vertically shifted for the sake of clarity.

nanostructured material, which can affect the recrystallization process.

CL spectra from Mn implanted bulk crystals are represented in Fig. 4(b). In this case, spectra from bulk are different from those from nanostructures implanted with Mn (Fig. 3(c)). In nanostructures, an intense broad band is observed centered around 450 nm, while in bulk this band is not so clearly observed. Fig. 5 shows CL spectra acquired at different excitation densities from the Mn implanted bulk sample after thermal annealing at 700 °C. Excitation density is modified by focusing and defocusing the electron beam incident on the sample. The low excitation density (defocused beam) results in a broadening to longer wavelengths of the UV-blue defect-related band. In fact, a band centered around 510 nm is observed, while for the higher excitation density the width is reduced and this band is not observed. Variations in the relative intensities of the bands when modifying the excitation density are usually related to saturation of specific radiative paths due to different transition lifetimes. The wavelength of this band is close to the range in which manganese usually emits in this oxide, although not exactly. An orange emission (590 nm) has been reported due to internal $^4T_1$–$^6A_1$ transitions in Mn^{2+} ($3d^5$) ions occupying the tetrahedral sites in nanowires that contain both monoclinic Ga_2O_3 and spinel phases ($MnGa_2O_4$) [25]. Mn doped Ga_2O_3 phosphor thin films show a luminescence band around 510 nm [26], which was assigned to Mn^{2+} ions. Lovejoy et al. reported XANES results which demonstrate that a mixture of Mn^{2+} and Mn^{3+} ions formed in octahedral sites of bulk Ga_2O_3 [27]. The presence of the 510 nm band in our samples could suggest that Mn ions in lower excitation states (Mn^{2+}/Mn^{3+}) form after the implantation and RTA processes. Future work will be needed to elucidate whether this band is directly related to the presence of Mn in gallium oxide.

4. Conclusions

In summary, β-Ga_2O_3 nanowires have been effectively doped with Cr or Mn by ion implantation. Their luminescence properties have been characterized. Thermal treatments in the range of 700 °C to 1100 °C temperatures have been performed in order to recover the lattice damage induced by ion implantation. The degree of improvement of the crystal quality after these thermal treatments has been studied by Raman spectroscopy and CL measurements. Raman analysis allowed examination of the correspondence between annealing temperature and crystal recovery, proving the effectiveness of the thermal treatments. Recrystallization starts around 700 °C and is complete at around 1100 °C. Besides, morphology has not been affected by the implantation or annealing treatments, as shown in the SEM images.

CL technique has been used to test the luminescence bands of the doped nanostructures and bulk samples. The evolution of the characteristic Cr red emission band with the annealing temperature agrees well with the evolution of the width of the Raman peaks in the nanostructured material. The lineshape evolution of the Cr emission is similar for both the nanostructured and the bulk material. Therefore, we could monitor the effective recrystallization of the implanted material from observation of the luminescence spectra. On the other hand, luminescence directly related to Mn ions cannot be clearly assigned. Ion implantation and partial recrystallization of the samples result in a broadening of the UV-blue band, assigned to defects created during this doping process.

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