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BRIEF COMMUNICATION

Synthesis and characterization of silicon-doped gallium oxide nanowires for optoelectronic UV applications

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Abstract Silicon-doped gallium oxide nanowires have been synthesized by thermal methods using either a mixture of gallium oxide and silicon powders or metallic gallium with silicon powder as precursor materials. The growth mechanism has been found to be a vapour–liquid–solid (VLS) or vapour–solid (VS) process, respectively, depending on the precursor used. In the former case, silicon oxide droplets at the end of the nanowires have been observed. Their possible role during the growth of the nanostructures is discussed. Structural and morphological characterization of the doped nanowires has been performed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The results show a high crystalline quality and a uniform distribution of silicon along the nanowires. Room temperature cathodoluminescence (CL) in the SEM shows that slight variations in the composed UV–blue emission band appear due to the influence of Si impurities in the oxygen vacancy defect structure.

Keywords Nanowire · Gallium oxide · Silicon · Dopant

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Introduction

Gallium oxide is an interesting transparent semiconductor oxide with a wide band gap (around 4.9 eV), which enables optical applications in the UV–visible range (Tippins 1965; Yu et al. 2002; Nogales et al. 2005; Nogales et al. 2007a). In the recent years, synthesis of gallium oxide nanowires by several methods has been reported for different applications, such as gas sensors and light waveguides (Feng et al. 2006; Arnold et al. 2009; Nogales et al. 2007b). In semiconductor oxides, high concentration of oxygen vacancies at room temperature is responsible for their electrical conductivity. These defects lead to donor levels into the forbidden band gap, which contribute to electron carriers and confer the semiconductor properties. They are also responsible for the luminescence properties (Binet and Gourier 1998; Yamaga et al. 2003). In order to use gallium oxide nanostructures as good candidates for optoelectronic applications, a control of the carrier concentration and conductivity type (n or p) is of paramount importance. In particular, two recent works have been devoted to the study of electrical and optical properties of bulk Ga_2O_3 single crystals doped with silicon (Shimamura et al. 2008, Víllora et al. 2008). An increase of three orders of magnitude of the electrical conductivity of Ga_2O_3 single crystals by intentional silicon doping has been reported (Víllora et al. 2008). Also, the variation of defects concentration (oxygen vacancies donors and gallium vacancies acceptors) by silicon doping has

been discussed through photoluminescence measurements (Shimamura et al. 2008). However, there is less information on silicon-doped gallium oxide nanowires or nanostructures and their influence on the defects structure. In fact, doping of nanowires is a difficult task because of their excellent crystalline quality with low structural defects and impurities tend to out diffusion to the surface. In the recent years, a high amount of work was devoted to the growth of undoped semiconductor nanowires by several approaches, but few works were directed to effectively doping of semiconductor nanowires. The techniques that are used to fabricate the nanowires (e.g., CVD, MBE, thermal evaporation, …) are mainly based on two growth mechanisms: vapour–solid (VS) and vapour–liquid–solid (VLS) (Barth et al. 2010; Lu et al. 2006). The latter presents the advantage of a higher control of the shape and size of the nanostructures. However, this mechanism needs foreign catalyst droplets to grow the nanowires and incorporation of a certain amount of catalytic atoms into the wires has been observed (Allen et al. 2008; Barth et al. 2010). This fact can pose some problems for a high control of doping of the nanowires. The VS method does not need a foreign catalyst and is based on the anisotropic growth of the crystals due to differences in surface energy of different planes, defects such as screw-dislocations or self catalysis (Barth et al. 2010). We have previously used a thermal method to obtain nanowires of some semiconductor oxides without the need of a foreign catalyst (Nogales et al. 2007b; Maestre et al. 2005; Hidalgo et al. 2007). In the present study, we apply this method to obtain a high number of Si-doped Ga_2O_3 nanowires and microstructures by using gallium oxide and metallic gallium in the presence of silicon, as starting materials. The Si-doped Ga_2O_3 nanowires were characterized by scanning and transmission electron microscopy, as well as by cathodoluminescence (CL) in the SEM. The possible role of silicon during the growth of the nanowires is discussed. The effective incorporation of Si atoms and their influence on the luminescence of the nanowires at room temperature are also discussed.

Experimental

Two different procedures were used to obtain Si-doped Ga_2O_3 nanostructures. In the first one, high purity gallium oxide powder (99.999%) was mixed with high purity silicon powder at 1.4 wt%, milled for 30 h at room temperature in air in a centrifugal ball mill (Retsch S100) equipped with hardened steel vial and 20 mm diameter agate balls. They were subsequently compacted into pellets and annealed at 1,500 °C for 15 h under argon flow. This sample is labelled G_1. Other temperatures (1,400 and 1,450 °C) as well as a higher silicon concentration (2.5 wt%) were also used to obtain structures and it was found that the results presented for sample G_1 are representative for this procedure. In the second procedure a pellet of pure gallium oxide was used as a substrate on which metallic gallium and silicon powders were placed and annealed at 1,250 °C for 8 h under an Ar flow. These precursors were not milled. This sample is labelled G_2. In this case, oxidation of metallic gallium and diffusion of Si atoms into the Ga_2O_3 nanostructures take place during the growth process. Undoped nanostructures were also studied for comparison. Transmission electron microscopy (TEM), high resolution TEM (HRTEM), selected area electron diffraction (SAED) and energy dispersive x-ray microanalysis (EDX) measurements were carried out in a JEOL JEM 3000F microscope to study the crystal properties of the obtained nanostructures. Scanning electron microscopy (SEM), CL and EDX measurements were performed in a Leica 440 Stereoscan scanning electron microscope. EDX results were obtained with a Bruker system.

Results and discussion

Figure 1 shows SEM images of the structures obtained in sample G_1. Terraced structures with square section are observed in Fig. 1a. Other flat microstructures ending by nanowires are also observed (Fig. 1b). The latter morphology is also obtained in undoped Ga_2O_3 nanostructures grown from pure gallium oxide compacted pellet as precursor (Nogales et al. 2005). The terraces shown in Fig. 1a, present hemispherical shaped droplets on their top that seem to drive their growth. In Fig. 1b, nanowires with a few hundred nanometers width and several micrometers length are shown, which also present these hemispherical droplets on their tips, as shown in the inset. This image shows that the growth

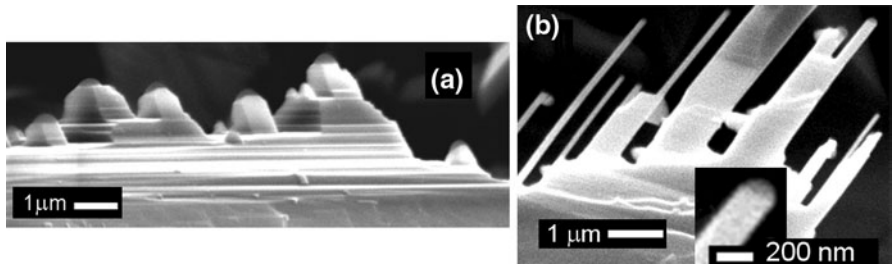

Fig. 1 SEM images of structures obtained in sample G_1. Hemispherical droplets at the wire ends are observed **a** at the top of terraces and **b** at the tip of the nanowires. *Inset* detail of the tip of one of the nanowires

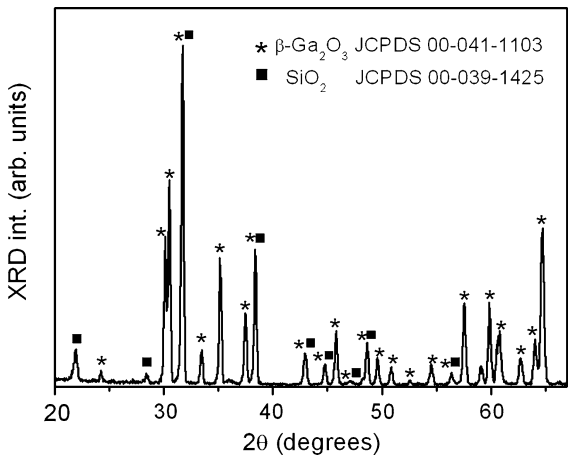

Fig. 2 XRD spectrum of the sample G_1

direction is the same for all these nanowires. This direction has been determined from the SAED and HRTEM results, as shown below. XRD spectra, shown in Fig. 2, demonstrate that, after the thermal treatment, only monoclinic gallium oxide and silicon oxide phases are present in the samples (JCPDS 00-041-1103 and 00-039-1425, respectively).

In order to determine the structure and composition of the nanowires and the droplets, TEM, HRTEM and EDX measurements have been carried out. Figure 3a shows the TEM image of the tip of a nanowire of sample G_1 with a diameter of 330 nm. The hemispherical droplet is clearly imaged and a truncated cone-shaped interface between the nanowire and the droplet is observed. HRTEM studies of the nanowires showed that they are monocrystalline. A HRTEM image of the nanowire is shown in Fig. 3b, where the growth direction is found to be (−110). The inset shows the SAED pattern, with zone axis (11-2). Local EDX spectra were obtained from the tip and from the nanowire, Fig. 3c. The spectra show that the Ga_2O_3 nanowire contains a small amount of silicon. Inset in Fig. 3c shows the Si $K_{\alpha 2}$ line observed in the Ga_2O_3 nanowire, which leads to a Si concentration of around 1 at.%. On the other hand, the EDX spectrum from the tip shows that is formed by silicon oxide, with diluted gallium. SAED analysis of the droplet (not shown) demonstrates that it possesses amorphous structure. The presence of droplets indicates that Si may play a catalytic role in the growth of the nanowires by a vapor–liquid–solid process.

Figure 4 shows SEM images of nanowires from sample G_2. A high density of nanostructures is obtained. The wires diameter range is between 100 nm and a few microns. Their morphology is similar to that of undoped gallium oxide structures obtained under the same conditions (Nogales et al. 2009).

No evidence of hemispherical droplets similar to those found in sample G_1 has been found in this sample, indicating that a VS growth mechanism was responsible for the formation of the structures. EDX images in the SEM for Si, Ga and O of the structure represented in Fig. 5a, are shown in Figs. 5b–d, respectively. The Si distribution along the structure can be considered fairly homogeneous. Quantitative analysis of Si K_α peaks from EDX spectra yields a content of around 1 at.% in the Ga_2O_3 nanostructures, which demonstrates the effective doping of these structures by the method used. The Si concentration is of the same order as in the case of the sample grown by the mixed powders method.

From these results, we can conclude that both methods used to obtain Si-doped nanostructures are equally valid. However, certain advantages are observed for samples obtained with the procedure followed to grow sample G_2. For example, lower temperatures and shorter times are needed during the process. Besides, a higher density of nanostructures is usually obtained with this method.

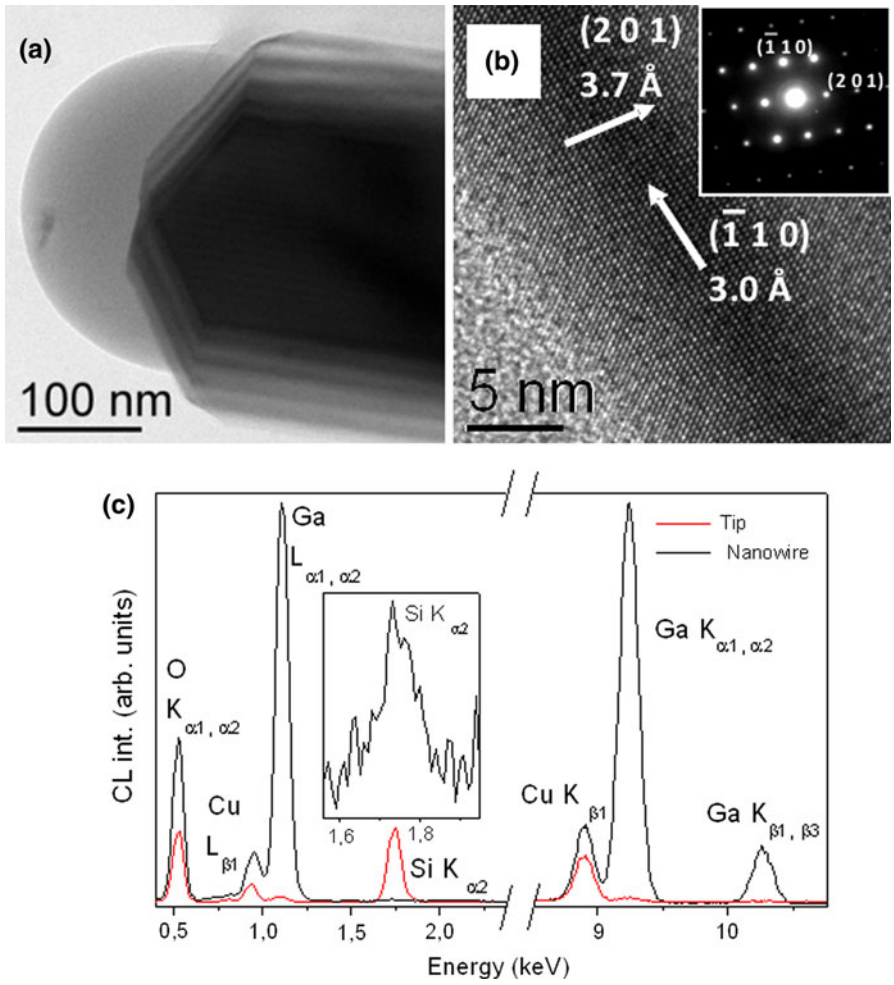

Fig. 3 **a** TEM image of a nanowire in sample G_1, showing the presence of an amorphous hemispherical droplet at its end. **b** HRTEM image of the same nanowire. *Inset* SAED pattern of this area. **c** EDX spectra of the droplet at the nanowire tip (*red line*) and the nanowire (*black*). Copper lines arise from the sample holder. Inset shows the Si $K_{\alpha 2}$ line observed in the nanowire, demonstrating that it is doped with a concentration around 1% at

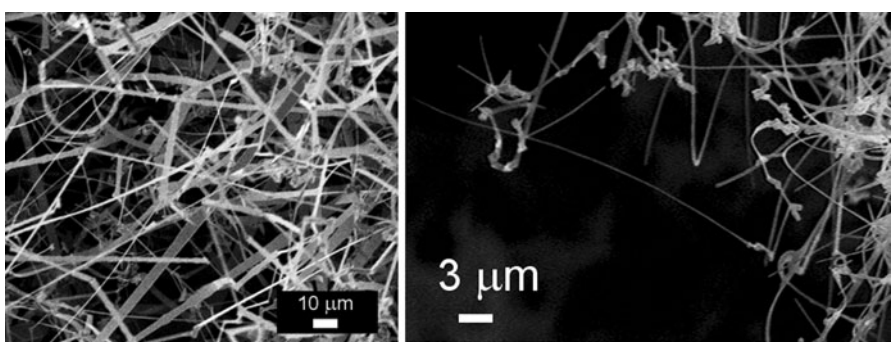

Fig. 4 SEM images of the structures obtained in sample G_2

When a mixture is used (G_1), a silicon oxide droplet appears at the tip of the gallium oxide nanowire. Besides, EDX analysis shows that silicon is incorporated into the nanowire, as explained above in the text. This fact would not be against the interpretation of the silicon oxide droplet behaving as a catalyst, because incorporation of catalytic material into the nanowires has been reported previously (Allen et al. 2008; Barth et al. 2010). In the case of nanowires obtained after oxidation of metallic gallium in the presence of silicon (G_2), a diffusion process takes place and Si impurities are added into Ga_2O_3 nanowires in a uniform way. The main difference between the two used procedures concerns

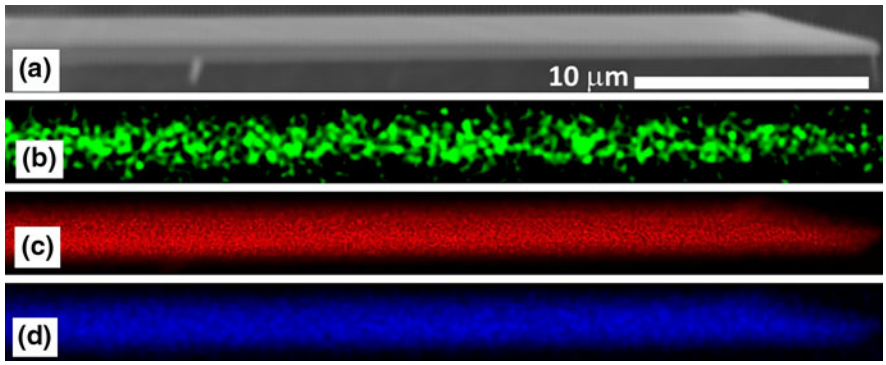

Fig. 5 **a** SE image of a structure from sample G_2 and the corresponding **b** Si, **c** Ga and **d** O, EDX maps

the specific morphology of the nanostructures developed in each case. In the case of G-2 samples the process yields a high amount of nanowires directly on the surface pellet, while for G-1 the nanowires have a silicon oxide droplet at the tip and grow from planar microstructures.

Let us now consider the comparison of the luminescence bands for undoped and Si-doped Ga_2O_3 nanowires. Figure 6 shows the room temperature CL spectra from undoped and Si-doped Ga_2O_3 nanostructures. As a common feature, they show a broad emission band in the blue–UV region, which can be deconvolved into two components centered at 3.1 eV (400 nm) and at 3.4 eV (365 nm), respectively. The CL spectrum of undoped nanowires (Fig. 6a) shows that the UV component at 3.4 eV is more intense than the blue one (3.0 eV), while for Si doped ones the component at lower energies dominates the spectrum. Hence, the result of Si doping is a red shift of the CL spectrum, due to the relative decrease of the UV component with respect to the blue one. This fact is more noticeable in G_1 samples, as it can be seen in Figs. 6b, c.

Blue–UV emission bands in the 2.8–3.4 eV range have been reported in the literature for undoped gallium oxide by photoluminescence (PL) (Binet and

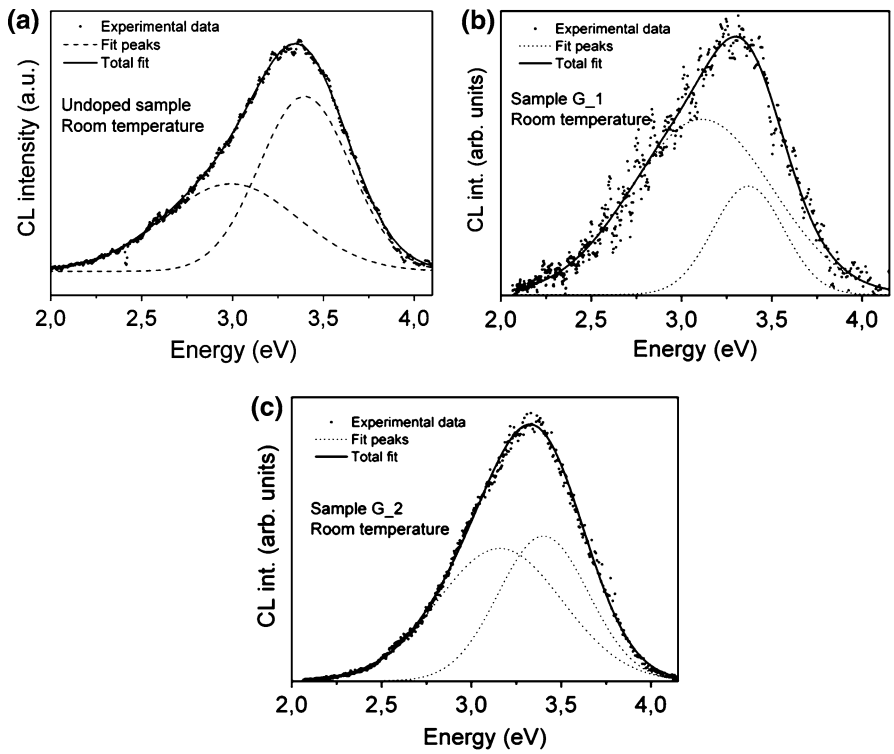

Fig. 6 CL spectra from **a** undoped Ga_2O_3 nanowires. **b** Si-doped G_1 nanostructures (structure show in Fig. 1b) and **c** CL spectrum from Si-doped G-2 sample (structure shown in Fig. 3)

Gourier 1998; Shimamura et al. 2008) and CL (Yu et al. 2002; Nogales et al. 2005; Borini et al. 2003) and were assigned to self-trapped excitons and donor–acceptor pair transitions. Oxygen vacancies (V_O) or Ga interstitials have been proposed as donors and $V_O - V_{Ga}$ pairs were supposed to be the acceptor centers (Binet and Gourier 1998; Harwig and Kellendonk 1978). In particular, Shimamura et al. (2008) studied the influence of Si doping on the luminescence of bulk β-Ga_2O_3 by PL at 10 K. They found a broad UV–blue band and observed a decrease of the total PL with silicon concentration, which was attributed to a decrease of V_O donors. In our study, the differences observed in the blue–UV luminescence in the studied samples can be explained by different concentration of the native defects and silicon impurities in Ga_2O_3-doped nanostructures. Undoped nanowires are expected to have a certain oxygen vacancies concentration, which leads to the observed CL bands, accordingly with the above mentioned models in the literature. By adding silicon impurities, a change in the native defects structure may occur, leading to a decrease in the UV/blue intensity ratio, as a common feature for G_1 and G_2 nanostructures. Moreover, differences between doped G_1 and G_2 samples can be explained by considering their specific doping process. For G_1 nanowires the growth seems to be driven by silicon particles leading to a droplet at the nanowires tip, as described above, and silicon segregation during the nanowires growth takes place. On the other hand, silicon diffusion into oxidized gallium seems to be the doping mechanism for G_2 nanowires. Although silicon impurities have been incorporated in a similar concentration in both cases, the interaction of V_O, V_{Ga} or Ga interstitials defects with Si may be different in each case. Therefore, the growth process of doped nanostructures is a key point, which determines not only the nanostructure morphology but also the defect structure and, hence, the luminescence properties.

Summary

In conclusion, Si-doped β-Ga_2O_3 nanowires have been obtained by two different procedures. In the first one, by thermal treatment of a mixture of silicon and gallium oxide powders, nanowires are grown by a VLS growth mechanism, with amorphous silicon oxide drops which could behave as catalyst. In the second one, nano- and microstructures have been obtained by thermal treatment of metal gallium and silicon. No catalyst drops are observed in this case, indicating a VS growth mechanism. Certain advantages are considered for the growth of the nanostructures with the second method. The dopant density is observed to be in the range of 1 at.% and uniform along the structures in both cases. CL studies show that, at room temperature, the presence of the impurities modifies the relative UV/blue components intensity ratio.

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