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Cathodoluminescence study of isoelectronic doping of gallium oxide nanowires

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ABSTRACT

Isoelectronic (In, Al) doped gallium oxide nanowires have been grown by a vapour solidification process. XRD and TEM were used for their structural characterization. The morphology and optical properties of the In(Al)-doped Ga_2O_3 nanowires have been investigated by means of the secondary electrons and cathodoluminescence (CL) techniques in the SEM. Red and blue-UV emission bands appear as complex bands and their components are influenced by the presence of In or Al, leading to a blue-shift of the blue-UV band usually observed in undoped gallium oxide. These In and Al related changes in the luminescence features of doped Ga_2O_3 nanostructures are discussed.

1. Introduction

Gallium oxide is a transparent conductive oxide with promising applications in the field of optoelectronics and gas sensing devices. It has a wide band gap (5 eV) and conducting behaviour due to its intrinsic native donor band related to oxygen vacancies. Investigations on optical properties of gallium oxide have been typically focused on Ga_2O_3 thin films. The wide band gap of Ga_2O_3 provides the possibility of light emission between the infrared and ultraviolet regions of the spectrum [1–3]. Undoped samples show green and blue-UV luminescence bands, which are related to native defects and may be affected by the growth conditions. Previous works reported the effect of specific impurities, such as several metal cations, in the luminescence bands in Ga_2O_3 thin films [4,5]. Moreover, as in the case of other oxides, low dimensional structures, such as nanowires or nanotubes, are also potentially useful in optoelectronic nanodevices [6,7]. In particular, we have studied in previous works the red luminescence due to the presence of Cr in the nanowires [2] and waveguiding behaviour of Er and Cr doped Ga_2O_3 nanowires [3].

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In this work, results concerning the growth of gallium oxide nanowires doped with isoelectronic atoms (In, Al) and their luminescence characteristics are reported. The aim is to study the influence of doping on the morphology and optical properties of Ga_2O_3 nanowires. As these atoms would occupy Ga sites in the Ga_2O_3 lattice, luminescence changes related to defects and/or electronic band structure are expected.

2. Experimental

Doped Ga_2O_3 nanowires have been grown by thermal evaporation under gas flow on the surface of a compacted pellet. The pellets were made from a mixture of Ga_2O_3 powder and 5% wt. or 10% wt. In_2O_3 (or Al_2O_3) powders. Thermal treatments were performed at 1500 °C for 15 h in a furnace under argon flow. The crystal properties of the samples were studied by X-ray diffraction (XRD) and high resolution-TEM (HRTEM). The morphology of the structures was characterized by scanning electron microscopy (SEM) in a Leica 440 Stereoscan microscope, which was also equipped with a cathodoluminescence (CL) system. The operating conditions used were 15–20 keV for the electron beam voltage, 1–5 nA beam current and liquid nitrogen temperature.

3. Results and discussion

XRD spectra revealed that the crystalline structure of In (Al) doped samples corresponds to the monoclinic phase of gallium oxide, β-Ga_2O_3. Neither In_2O_3 nor Al_2O_3 related diffraction peaks are detected, which indicates that In or Al atoms should be incorporated into the β-Ga_2O_3 lattice.

SEM images from In doped Ga_2O_3 show the formation of flat surfaces with steps and terraces of decreasing size. A representative SEM image of samples with 5% wt. of In oxide is shown in Fig. 1a. This morphology is similar to that developed in undoped samples [1]. In the case of 10% In, longer nanowires grow from rods formed on the surface of the pellet as it is shown in Fig. 1b. SEM images from Al doped β-Ga_2O_3 also show the formation of flat surfaces with wires of decreasing cross-section along the growth axis (Fig. 2). The inset shows a detail of a single nanowire with a diameter of 136 nm.

In order to assess the crystal quality of the doped samples, HR-TEM measurements were performed. Fig. 3 shows a high resolution TEM image from a 5% Al doped nanowire. Interplanar distances are 0.24 and 0.31 nm along directions *a* and *b* indicated in the figure, which corresponds to (401) planes of the crystal structure of β-Ga_2O_3. Electron diffraction pattern leads to a [010] zone axis. HR-TEM analysis show as well the high crystal quality in In doped β-Ga_2O_3 nanowires. Energy dispersive microanalysis confirms the presence of indium or aluminium in the corresponding nanowires.

Cathodoluminescence measurements from nanostructures enable us to study the influence of doping on the optical properties of the obtained nanostructures. As β-Ga_2O_3 is a wide band gap semiconductor the presence of impurities may originate luminescence bands or peaks in the studied range. CL spectra from In or Al doped β-Ga_2O_3 with highest dopant content are shown in Fig. 4, which display red and blue-UV bands. The narrow red luminescence peaks are due to chromium impurities (2, 3) and usually dominate the luminescence features in β-Ga_2O_3 nanowires, when comparing with thin films. A strong and broad blue-UV band above 3 eV is observed in both doped samples. For In doped samples, it is centered at 3.2 and at 3.5 eV for Al doped samples. Previous works on gallium oxide have reported a blue-UV band at 3.1 eV [4]. Therefore, a blue-shift of this band is revealed for In and Al doped Ga_2O_3 and the shift is higher in the case of aluminium doped samples.

The blue-UV band has been attributed to donor-acceptor-pairs (DAP) transitions involving oxygen vacancies as donors and other structural defects or impurities as acceptors. The detailed origin of these emissions is not completely understood and several models for defects or complexes have been proposed in the literature [4,5,8], in which is well accepted that oxygen vacancies play a key role in the luminescence mechanisms in gallium oxide. For example, an increase of a green–blue emission has been observed under O-rich growth conditions in high purity crystals [5] and UV emissions were found to be independent on the growth conditions [4]. Ga interstitials have been proposed as donors

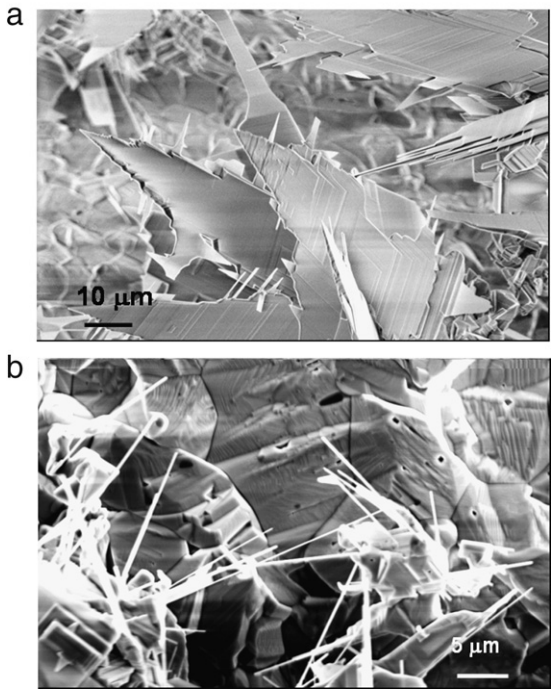

Fig. 1. SEM images of In doped β-Ga_2O_3 nanostructures grown from a mixture with (a) 5% wt. In_2O_3, and (b) 10% wt. In_2O_3.

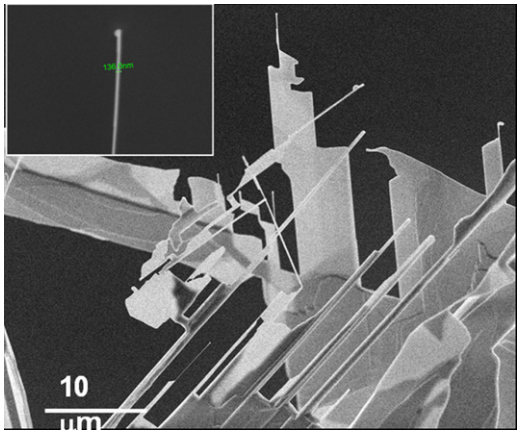

Fig. 2. SEM image of Al doped β-Ga_2O_3 nanostructures. Inset: Detail of a single nanowire with a diameter of around 130 nm.

and (V_O, V_{Ga}) pairs as acceptors [8] in undoped samples. The addition of metallic impurities can induce a predominant either blue or green emission when cations have a larger or lower ionization charge than three, respectively [9].

A recent work [10] suggests a model for blue-UV bands in pure and Si-doped β-Ga_2O_3. The authors reported two UV bands and one blue band at 3.6, 3.1 and 2.5-2.8 eV, respectively, and suggested that acceptor defects with ground state close to the valence band are involved in UV emissions.

Therefore, the present luminescence results confirm that the incorporation of specific impurities may modify the native defect structure. Besides, in the case of the nanowires a very low green

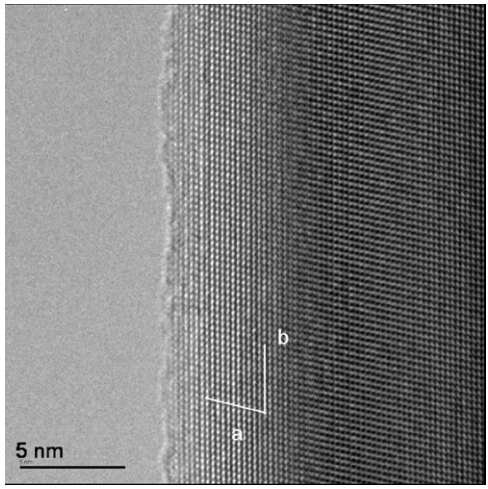

Fig. 3. High resolution TEM image of Al doped β-Ga_2O_3 nanostructures. Interplanar distances are indicated with arrows.

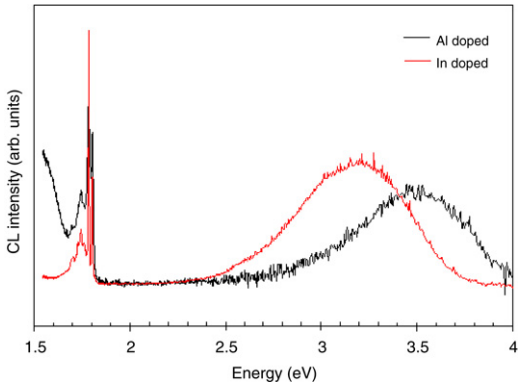

Fig. 4. CL spectra from In and Al doped β-Ga_2O_3 nanowires.

component is detected in our CL spectra, suggesting that the oxygen vacancies concentration seems to be lower than in bulk or thin films samples. Our scenario refers to isoelectronic doping in which In may occupy Ga sites in the crystal lattice and modify the structure of the Ga-related defects, such as V_{Ga} or Ga interstitials, leading to the strong observed blue shift in the blue-UV band in In (Al) doped β-Ga_2O_3 nanowires.

4. Conclusions

In or Al doped β-Ga_2O_3 nanowires were grown by a vapour-solidification process using the corresponding binary oxides as precursor materials. Indium doping leads to similar nanowires and microstructures to that obtained in undoped Ga_2O_3, however Al-doped Ga_2O_3 presents rods with stepped surfaces and plates. The nanowires show a high crystal quality through the TEM analysis. The incorporation of isoelectronic impurities modifies the luminescence of the wires, as demonstrated by the CL results. The blue-UV band in In or Al doped β-Ga_2O_3 is blue-shifted 0.2 and 0.4 eV respectively, when comparing with undoped samples. This strong blue-shift suggests that oxygen vacancies and gallium related defects have been modified due to the doping process.

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