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Epitaxial growth of luminescent Sn-Cr doped β-Ga_2O_3 nanowires

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ABSTRACT

Elongated micro- and nanostructures of Sn doped or Sn and Cr co-doped monoclinic gallium oxide have been grown by a thermal method. The presence of Sn during growth has been shown to strongly influence the morphology of the resulting structures, including Sn doped branched wires, whips, and needles. Subsequent co-doping with Cr is achieved through thermal diffusion for photonic purposes. The formation mechanism of the branched structures has been studied by transmission electron microscopy (TEM). Epitaxial growth has been demonstrated in some cases, revealed by a very high quality interface between the central rod and the branches of the structures, while in other cases, formation of extended defects such as twins has been observed in the interface region. Cathodoluminescence (CL) measurements show a Sn-related complex band in the Sn-doped structures. In the Sn−Cr co-doped samples, the characteristic, very intense Cr^{3+} red luminescence emission quenches the bands observed in the Sn doped samples. Branched, Sn−Cr co-doped structures were studied with microphotoluminescence imaging and spectroscopy, and waveguiding behavior was observed along the trunks and branches of these structures.

INTRODUCTION

Monoclinic β-Ga_2O_3 is a transparent conductive oxide (TCO) with high thermal and chemical stability and controllable n-type conductivity with suitable doping. Impurities in semiconductor matrixes are key factors for improving electrical conductivity, supplying mobile carriers or introducing electronic traps in the band gap, which influence not only their electrical but also their optical properties. Besides the tuning of its physical properties, the control of the dimensionality and morphology is also relevant for the applications of semiconductor oxides in areas of nanoscience and nanotechnology[1, 2]. This point has been less explored, and the control of the nanostructures morphology by the addition of impurities during the growth process is worth investigating. Regarding its electrical and optical properties, Ga_2O_3 behaves as an n-type semiconductor due to the presence of a donor band related to intrinsic defects and/or native impurities[3, 4] and is transparent in the blue-UV range. An effective tuning of electrical or optical properties by the addition of impurities in oxide nanowires is still a challenge, because of the out-diffusion processes and, in many cases, of the low diffusivity of the impurities in nanowires[5].

EXPERIMENTAL SECTION

The Sn doped β-Ga_2O_3 structures were grown by thermal oxidation at 1100 °C of metallic Ga in the presence of SnO_2 under an inert gas flow on a Ga_2O_3 pellet used as substrate[6].

The morphology of the doped structures is influenced by the presence of tin during growth resulting for example in the formation of branched structures. In a second stage, the rest of the structures were used as starting material to obtain co-doped (Sn,Cr)-Ga_2O_3 branched structures by a further thermal treatment at 1500 °C for 15 h in the presence of chromium oxide powders. Selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) were performed in a JEOL 3000 FEG electron microscope, fitted with a double tilting goniometry stage (±22°, ± 22°). Energy dispersive X-ray microanalysis spectroscopy (EDS) and cathodoluminescence (CL) measurements were carried out in a Leica Stereoscan 440 SEM. Photoluminescence (PL) spectroscopy and imaging, have been performed in a Horiba Jobin Ybon LabRam HR800 Raman confocal microscope. The excitation light was the 325 nm line of a HeCd laser. All PL measurements were performed at room temperature. Raman measurements and XRD were also performed to assess the crystal quality of the wires.

DISCUSSION

Influence of Doping on Morphology and Crystalline Structure

The Sn doped structures present a branched shape with trunks whose lengths can reach several hundred micrometers and widths in the range of a few hundred nanometers up to a few micrometers. The branches tend to reach up to several micrometers in length and have widths in the range of a few hundred nanometers. XRD measurements (not shown) of Sn doped complex structures show that the crystal structure of the nanowires mesh is the monoclinic β-Ga_2O_3 (JCPDS 00-041-1103). No peaks corresponding to other phases are found.

Low magnification bright-field TEM images of such structures are depicted in Figure 1. They have nanobelt shape with average lateral size of around 1 μm. Figure 1a shows a nanobelt with a tin ball, which was found to be amorphous, at its end. This shows the existence of a metal catalyzed vapor−liquid−solid (VLS) growth mechanism2. The EDS microanalysis performed within the TEM shows that the chemical composition of this droplet is Sn. In the VLS mechanism the metal particle size usually determines the wire diameter, but in our case, the width of the belt does not perfectly fit to the tin ball diameter. On the other hand, tin balls have also been observed attached to the lateral surface of the belts as Figure 1b shows. The inset in Figure 1b shows the detail of the final end of the belt with a flat shape. These results support that tin could play a catalyst-like role in order to develop elongated structures. However, as tin particles are formed not only at the end of the wires, but also at lateral points along the main trunk, branched structures are formed, as observed.

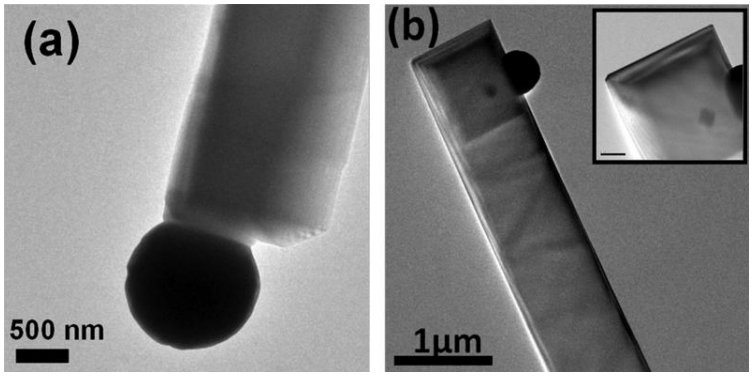

Figure 1. Low magnification bright-field TEM images of Sn doped Ga_2O_3 wires: (a) a nanowire with a Sn ball in its tip and (b) nanoribbon shaped structure. The inset shows the morphological shape of the nanostructure end.

In order to characterize the crystal quality of Cr doped branched structures after the Cr diffusion process, some samples were studied by TEM. Figure 2a shows the low magnification TEM image of one of these branched structures, where a junction of a trunk and a branch marked by arrows in the figure, is observed. The SAED along the [100] zone axis corresponding to the branch is depicted in Figure 2b. The HRTEM image at higher magnification of the same area (Figure 2c) shows a very well crystallized material. No structural defects are present. The measured interplanar distances are 3.03 and 5.79 Å, which fit well to the b and c parameters of the β-Ga_2O_3 unit cell, respectively. The growth direction obtained from this image is [001]. EDS microanalysis performed on this branch shows a very homogeneous chemical composition and confirms the presence of Sn and Cr.

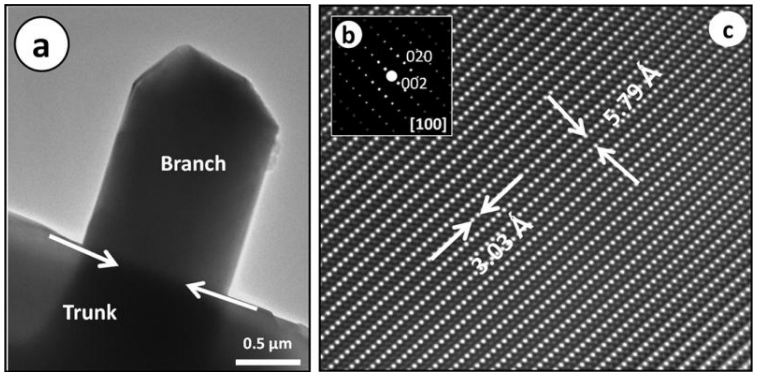

Figure 2. (a) Low magnification TEM image of a junction of a trunk and a branch in a branched structure. (b) SAED pattern along the [100] zone axis and (c) and the corresponding HRTEM micrograph.

Figure 3a shows a HRTEM image of a junction area, where two different crystal orientations are observed, that corresponds to the trunk and the branch, respectively. The FFT pattern along [201] (Figure 3b) was obtained from the trunk. Its I-FFT shows a contrast due to heavy atom positions and typical interplanar distances (3.03 and 3.33 Å) of the monoclinic β-Ga_2O_3 phase (Figure 3c). On the other hand, the FFT pattern of the branch is depicted in Figure 3d, which can be indexed along the [100] zone axis. The corresponding I-FFT image (Figure 3e) shows the interplanar distances a = 3.03 and c = 5.79 Å. Finally, the FFT pattern (Figure 3f) of the junction area (marked by dashed arrows in Figure 3a) reveals the overlapping of the

diffraction spots of both branch and trunk FFT patterns, which reveals a good match between both crystal orientations. The first layers of the branch seem to adjust quite well, suggesting a good epitaxial growth of these branched structures and a very high crystal quality. It should be noticed that actually, during the Cr diffusion process, no extra tin was incorporated into the furnace, and only chromium oxide powders were added for doping purposes. The Sn doped branched morphology is retained after the doping process, although an overgrowth of the structures is achieved, as we have already shown. This TEM analysis indicates that epitaxial growth is responsible for the growth of some branches in these samples. In other cases, however, the growth of branches is related to the formation of extended defects, such as twins. In all cases, the branches present very high crystal quality.

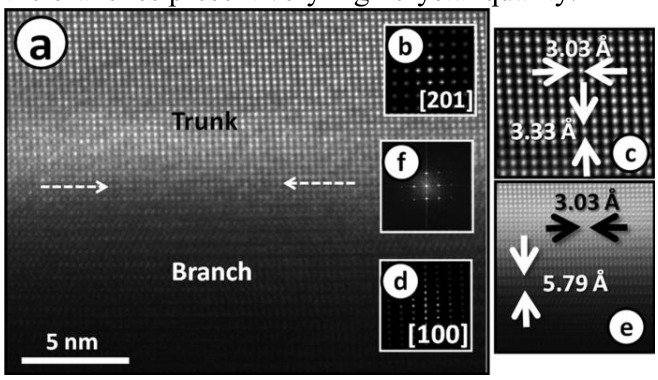

Figure 3. (a) HRTEM image of the interface region marked in Figure 2. (b) FFT pattern of the trunk along the [201] direction (c), and corresponding I-FFT. (d) FFT pattern along [100] direction of the branch and (e) corresponding I-FFT (e). At the interphase (marked by dashed arrows) the overlapping between both of the FFT patterns is seen in part f.

Influence of Doping on Luminescence Properties of Branched Structures.

We have assessed the effect of Sn doping in the optical properties of Ga_2O_3 branched structures by cathodoluminescence (CL) in the SEM. Figure 4a plots the room temperature (RT) CL spectrum from a bunch of Sn doped nanowires. A CL spectrum from undoped nanowires is also included for comparison. In spite of the low Sn concentration in the wires, a broad band in the whole visible range is observed, in clear contrast with the undoped wires, in which a narrower characteristic β- Ga_2O_3 UV-blue emission is obtained[8]. Figure 4b shows the Gaussian deconvolution of the CL spectrum shown in Figure 4a, with three main components centered at 2.4, 3.1, and 3.4 eV. The 3.1 and 3.4 eV bands are well-known in β-Ga_2O_3 and have been assigned to intrinsic defects, such as oxygen vacancies, or some very low concentration of impurities[3, 8]. The green band (2.4 eV) would be related to the presence of Sn in the wires which agrees with some previous reports. In particular, Miyata et al. obtained by electroluminescence in Sn doped Ga_2O_3 films a similar broad emission with a main peak at around 450 nm and a shoulder with its maximum in the green region[9], which resembles the spectrum observed by CL in our experiments. Maximenko et al. have also reported a broad visible emission in Sn doped Ga_2O_3 nanowires with a main peak at around 400 nm with a shoulder in the green region[10], which they attribute to recombination between donor levels, introduced by the incorporation of Sn atoms, and holes at the valence band in Ga_2O_3. These results show the high quantum

efficiency of Cr ions' emission, even at room temperature, in gallium oxide hosts, which led to the quenching of the green and the violet-blue emissions which are in competition with the Cr^{3+} intraionic transition. The very high efficiency of Cr ions quenches the radiative transitions between energy levels related to native defects in Ga_2O_3.

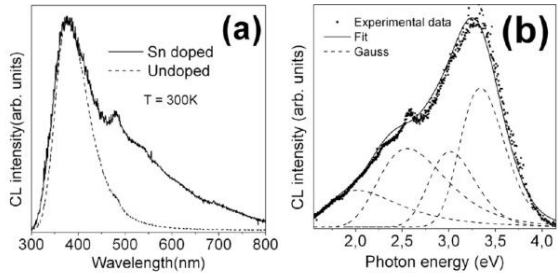

Figure 4. (a) CL spectra at RT from Sn doped sample and undoped β-Ga_2O_3 sample. (b) Detail of the composed bands in Sn doped Ga2O3 structures.

We have used the co-doped samples to study the propagation that the red light generated by Cr ions follows through these branched structures. Figure 5a shows the micro-PL spectrum from a Sn, Cr co-doped wire. In this case, the 325 nm (3.82 eV) HeCd laser line of the confocal microscope produces below band gap excitation, and strong red emission due to the Cr^{3+} intraionic transitions is observed. Excitation of the Cr^{3+} is indeed obtained through the excitation band centered at around 3.9 eV present for this ion in β-Ga_2O_3[7]. Figure 5b shows the corresponding visible μ-PL image of the wire. Under illumination with the laser at the upper end of the wire (violet arrow), the intense luminescence created is guided along the trunk and also transmitted through the perpendicular branch, as is clearly seen in the bright red spot highlighted with a white arrow in Figure 5b. UV laser radiation is also guided along the trunk and branch, as seen in Figure 5c for the 325 nm line of the laser. As shown in the CL spectra, the luminescence of β-Ga_2O_3 nanowires covers the whole visible range, and the emission wavelength can be adjusted by properly selecting the kind and concentration of dopants. In fact, doping of these branched structures with other optically active ions in order to obtain luminescence from the UV to the IR is possible by other doping methods such as ion implantation[11]. Besides, the branched morphology can be very useful for some specific applications such as photonic routers and beam splitters[12, 13, 14].

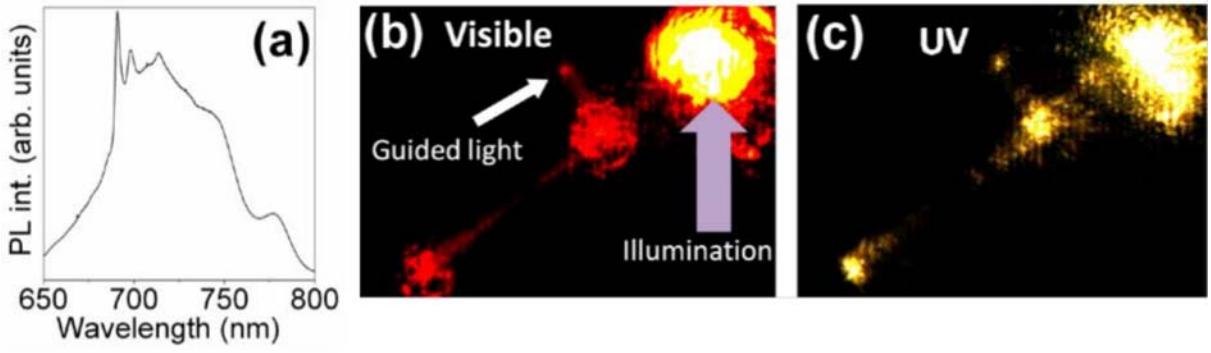

Figure 5. (a) PL spectrum from a branched wire. (b) Room temperature μ-PL with a 325 nm HeCd laser line excitation of the same branched structure. (c) UV radiation bright field image.

CONCLUSIONS

Elongated Sn doped gallium oxide structures have been obtained through a thermal evaporation method. The presence of Sn leads to the formation of branches. In a further thermal step, the branched structures have been co-doped also with Cr. The crystal quality has been found to be very high by TEM− HRTEM analysis, and the mechanisms for the formation of the branches have been discussed, finding epitaxial growth as one of them. Luminescence in the whole visible range is obtained by co-doping with Sn and Cr. For the first dopant, a broad emission covering most of the visible range is observed by CL, with strong peaks in the UV-blue and green ranges. When co-doping with chromium, the luminescence is virtually composed exclusively by the intense red band characteristic of Cr^{3+} in this oxide. Branched, Sn, Cr co-doped structures behave as efficient waveguides along their trunks and branches, both for the UV and visible light, as observed with microphotoluminescence imaging.

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