

Sn doped GeO₂ nanowires with waveguiding behavior

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 Nanotechnology 19 455705

(<http://iopscience.iop.org/0957-4484/19/45/455705>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 147.96.14.16

The article was downloaded on 20/02/2013 at 18:59

Please note that [terms and conditions apply](#).

Sn doped GeO₂ nanowires with waveguiding behavior

P Hidalgo¹, B Méndez and J Piqueras

Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, 28040, Spain

E-mail: phidalgo@fis.ucm.es

Received 17 July 2008, in final form 31 August 2008

Published 9 October 2008

Online at stacks.iop.org/Nano/19/455705

Abstract

Sn doped GeO₂ nanowires and microwires have been grown by an evaporation–deposition method, using a mixture of Ge and SnO₂ powders as precursors. Comparison with undoped GeO₂ nanowires grown by the same method shows that the presence of Sn prevents the formation of sharp bends, which makes the wires more suitable for waveguiding applications. Incorporation of about 0.5 at.% of Sn into the wires influences their morphology and gives rise to wires showing two different cross-sectional dimensions along the growth axis. Sn does not influence the luminescence spectra in the visible range but causes the appearance of emission bands in the near-infrared range. The waveguiding behavior of the Sn doped wires for green and red laser light has been demonstrated.

1. Introduction

Germanium dioxide, GeO₂, is a wide band gap material with several optical properties of interest in the field of optoelectronics. As in the case of other oxides, low-dimensional structures of GeO₂, such as nanowires or nanotubes, are potentially useful in nanoelectronic applications or optical nanodevices. In particular, wires of this material have good waveguiding properties due to its refraction index of 1.67 [1]. GeO₂ nanowires have previously been grown by different methods such as physical evaporation of Ge [2], laser ablation [3], thermal oxidation [4], thermal deposition [1, 5] and others. In [1], GeO₂ nanowires and submicron wires were grown by thermal treatment of compacted Ge powder under argon flow. This method, the growth of nanostructures on the surface of a pellet of compacted powder during thermal treatment, has previously been applied by our group to fabricate wires of different oxides [6–9].

Doping of nanostructures aimed at influencing the electronic and optical properties has been often reported. In particular, Sn can enhance the conductivity or improve the field emission properties of ZnO nanowires [10], and it is used to fabricate nanowires of the transparent conductor indium–tin-oxide [11, 12]. In addition, the presence of Sn has been found to influence the morphology of ZnO wires grown by thermal methods [10, 13]. Contrary to the case of other oxides, doping

¹ Author to whom any correspondence should be addressed.

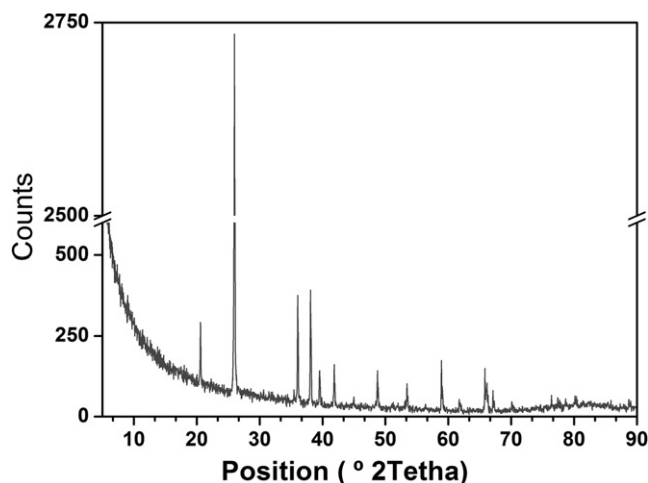


Figure 1. XRD spectrum of the nanowires showing α -GeO₂ structure.

of GeO₂ nanowires has been seldom reported, one instance being the work of Wu and Coffey regarding Er doping [14].

In this work Sn doped GeO₂ nanowires and microwires have been grown by using a mixture of Ge and SnO₂ powders as precursor for the above-mentioned thermal process. The presence of Sn causes a reduction of the cross-sectional dimensions of the wires and leads to a morphology which

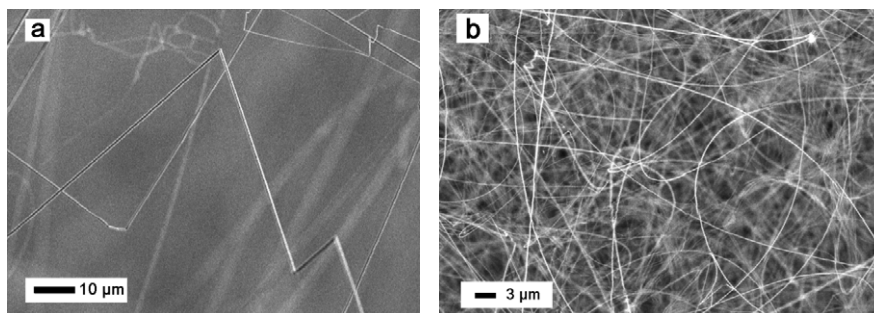


Figure 2. (a) SEM image of undoped GeO₂ wires formed by segments which show well defined angles. (b) SEM image of Sn doped GeO₂ wires showing no sharp bends.

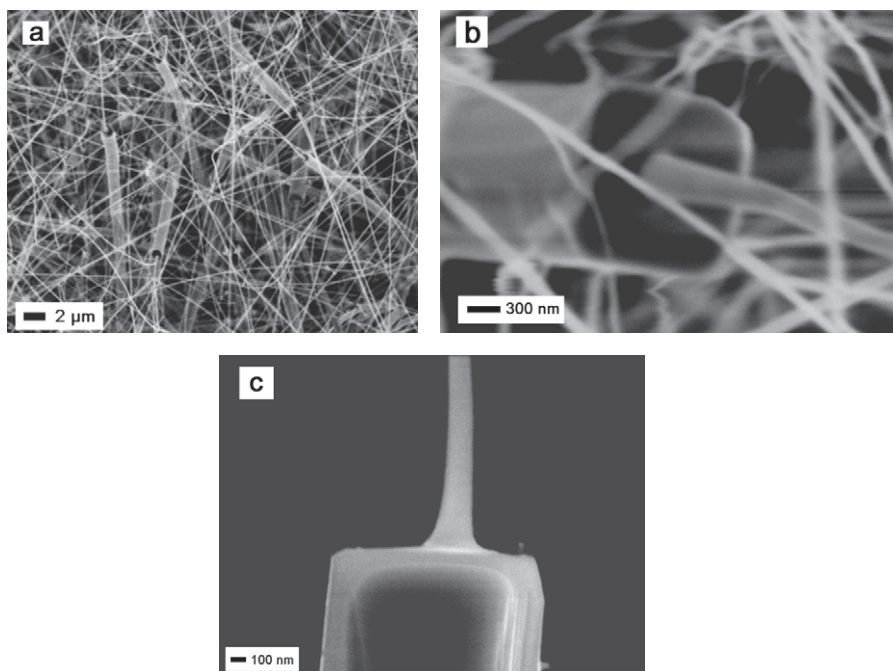


Figure 3. (a) SEM image of an area containing several stepped wires. (b) and (c) SEM images of the transition region from a large to a small cross-section in two wires.

favors waveguiding applications by preventing the formation of sharp bends. The doped wires have been characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), cathodoluminescence (CL) in SEM, transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS). The waveguide behavior of the wires was studied by illumination with light of different wavelengths.

2. Experimental details

The starting materials used were Ge powder and SnO₂ powder with purities of 99.999% and 99.9%, respectively. Ge–SnO₂ powders containing 1 and 10 wt% respectively were prepared by milling the corresponding mixtures in a ball mill (Retsch S100) with 20 mm agate balls for 5 h. The powder was compacted under a compressive load to form disk shaped samples of about 7 mm diameter and 2 mm thickness, which were then annealed at 600 °C for 6 h under argon flow. The furnace was not sealed for vacuum conditions, so air leaking into the furnace acts as a source of oxygen.

XRD measurements were performed with a Philips diffractometer. Secondary electron, EDS and CL measurements were carried out in a Leica 440 SEM and a Hitachi 2500 SEM. The CL measurements were carried out at liquid nitrogen temperature with a beam energy of 15–20 kV with a Hamamatsu R928 photomultiplier, a Hamamatsu R5509-43 cooled photomultiplier and a Hamamatsu PMA-11 charge coupled device camera. The EDS measurements were carried out with a Bruker AXS QUANTAX system. TEM observations were performed with a Jeol JEM 2000 FX microscope. For the waveguide measurements with an optical microscope, nanowires and microwires were glued at the end of a commercial light guide of 100 μm diameter, which guided 640 or 535 nm laser light.

3. Results and discussion

In all samples, the thermal treatment causes the growth of a dense distribution of nanowires on the disk surface. XRD of the wires shows the (101) peak of the hexagonal α-GeO₂ structure

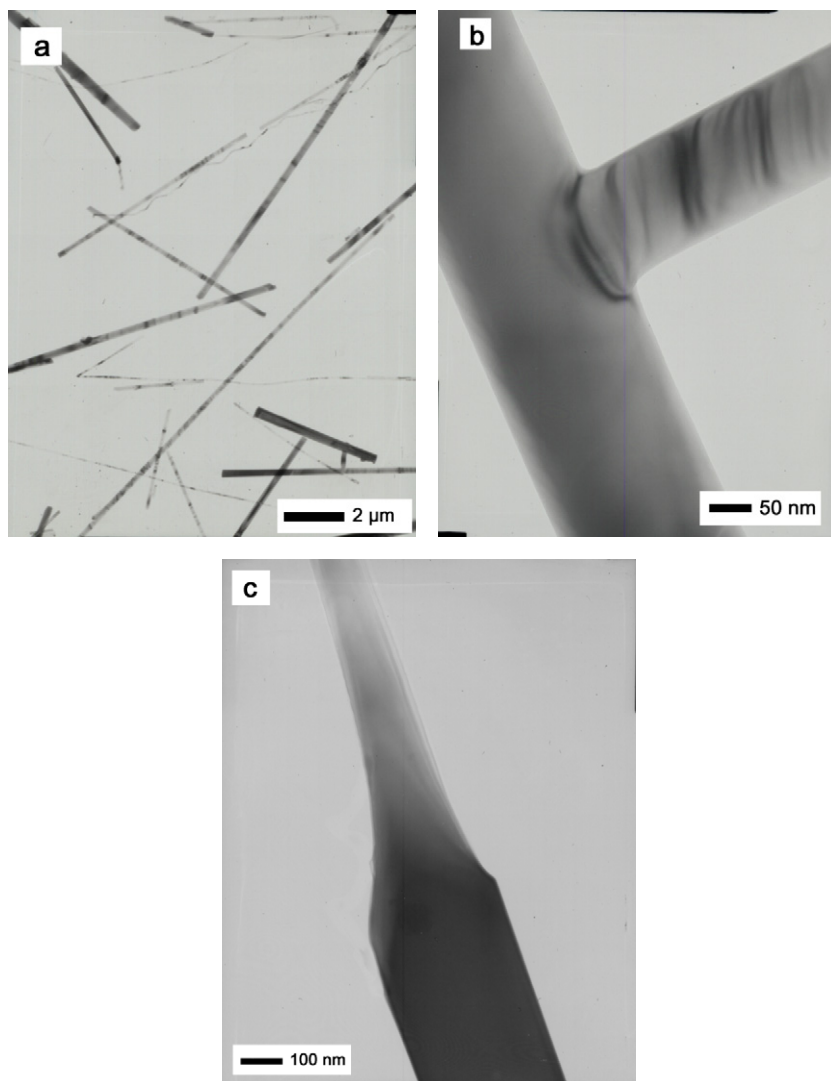


Figure 4. TEM images of (a) nanowires (b) a junction of two nanowires, (c) the first stage of the formation of the reduction of cross-section in a wire.

as the main peak of the spectra (figure 1) while no peaks related to the presence of Sn or Ge have been observed.

Doping with Sn has a clear influence on the morphology of the wires obtained. As previously reported [1], most of the wires grown from pure Ge powder have a four-sided cross-section with typical dimensions in the range 600 nm to 1 μm, and frequent sharp bends along their path (figure 2(a)). The wires in the sample grown from the powder containing 1 wt% SnO₂, by using the same treatment, have lengths of up to hundreds of microns, a much smaller cross-section, typically in the range 100–150 nm, and show no sharp bends, which would favor their application as waveguides (figure 2(b)). By increasing the amount of Sn, as in the sample prepared from powder containing 10 wt% of SnO₂, wires with a new and complex morphology grow. In particular, a large number of wires is observed in which a sharp cross-section reduction, from about 700–900 to 80–200 nm, takes place at a certain position of the growth axis. Figure 3(a) shows an area containing several of the stepped wires and figures 3(b) and (c) show the transition region from a large to a small cross-section

in two wires. The growth of the wires continues for long distances, hundreds of microns, from the step, and usually the wires become thinner with increasing distance.

Figure 4 shows TEM images of the nanowires. Figures 4(a) and (b) show respectively nanowires and a junction of two nanowires in the sample grown with 1 wt% SnO₂. Figure 4(c) shows the first stage of the formation of the reduction of cross-section in a wire of the sample grown with 10 wt% SnO₂. Electron diffraction patterns of the wires show that they are single crystalline. Since GeO₂ becomes amorphous after a short time under the microscope electron beam, more detailed TEM observations could not be performed.

As described above, Sn prevents the formation of sharp bends which are typical of the undoped wires. TEM of the undoped wires shows the presence of twin boundaries parallel, or nearly parallel, to the growth axis [1], so a change of the twin plane would involve bending of the nanowire. The absence of bends in the Sn doped wires can be explained if Sn causes an increase of the twin boundary energy, leading to wires with

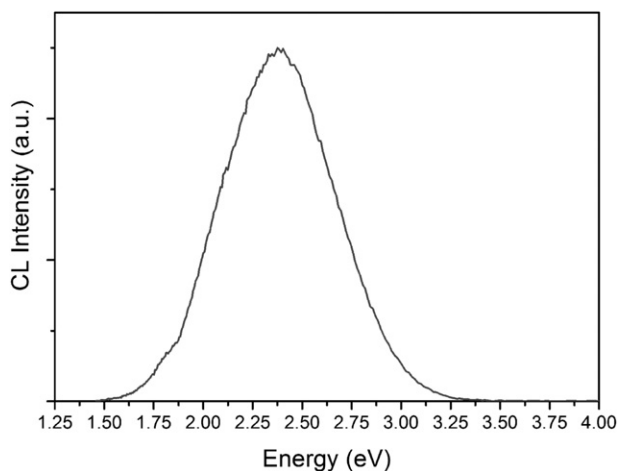


Figure 5. CL spectrum at 77 K of the Sn doped wires in the visible range.

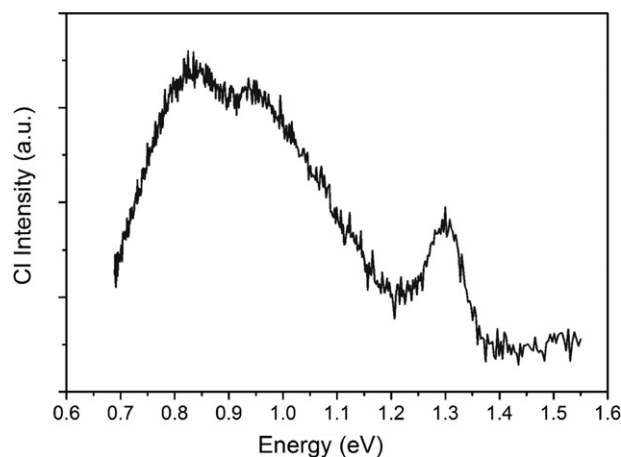


Figure 6. CL spectrum at 77 K of the Sn doped wires in the infrared range.

fewer boundaries. In fact, no twin boundaries were observed by TEM in the Sn doped wires. Impurities are known to influence the twin boundary energy of crystals, either causing an increase or a decrease depending on the specific impurity and the host. Since there are no data on the system $\text{GeO}_2\text{:Sn}$, we mention the influence of Sn on the twin boundary energy only as a possible effect.

The influence of Sn, and other impurities, such as In, on the growth direction and final morphology of elongated structures of oxides has been previously studied in ZnO. Li *et al* [15] found that Sn doped ZnO nanowires grown by a vapor–liquid–solid (VLS) process with Au catalyst have smaller diameters and longer lengths, and explain this observation by the small size of Sn–Au droplets formed on the substrate. In this work no catalyst has been used, and the nanowires grow directly on the surface of the compacted pellet. No metal drops have been observed at the top of the wires, which shows that the growth takes place by a vapor–solid (VS) rather than a VLS process. Surface segregation of Sn has been suggested by Wen *et al* [16] to induce the growth of side branches in Sn doped ZnO nanowires, in a VS process. Branched ZnO nanowires with two-, four- and six-fold symmetry have been grown by evaporation–condensation methods of ZnO– SnO_2 and ZnO– In_2O_3 powder mixtures [16–19]. The symmetry of the branched structure depends on the symmetry of the central nanowire so that, for instance, a six-fold array grows from a central nanowire which has hexagonal cross-section bounded by six equivalent surfaces. The lateral growth takes place by a VS or VLS process involving preferential Sn segregation or formation of Sn droplets on the lateral faces. In the present work, Sn does not lead to a hierarchical nanowire structure, which, to our knowledge, has not been reported for the case of GeO_2 , but favors growth along the axis, instead of growth on the lateral surfaces, resulting in thinner wires. This possibility is supported by the formation of wires with two different cross-sections, such as those shown in figure 3, in which the growth is favored on a specific region of the growth front. The mechanism leading to the thin wire arising from the front face

would be similar to that of the lateral growth in the above-described branched structures. An enhanced Sn segregation at some point of the growth front would lead to further growth of a thinner wire. Energy-dispersive spectroscopy (EDS) measurements confirm the presence of Sn in the wires. The typical Sn content in the large growth front of the two different cross-section wires was found to be in the range 0.4–0.6 at.%, which shows that only a small fraction of the Sn content in the starting mixture, which was 7.9 at.%, is incorporated into the GeO_2 wires, but this fraction has a marked influence on the wire morphology.

Due to the absence of sharp bends and their small cross-section, the Sn doped GeO_2 wires are, in principle, suitable as nanosize waveguides. However, the introduction of impurities may modify the luminescence properties of the material, leading in some cases to internal luminescence in the fiber so that the luminescence emission, rather than the excitation light, propagates along the fiber. CL measurements show that this effect does not take place in the case of $\text{GeO}_2\text{:Sn}$ in the visible range. Figure 5 shows the CL spectrum of the Sn doped wires in the visible range, with a broad band peaked at about 2.44 eV, which is similar to the spectra of undoped GeO_2 nanowires and nanoneedles [1, 5]. In contrast, the presence of Sn has been found to induce near-infrared luminescence in the wires. The spectrum of figure 6 shows infrared bands in the sample prepared with a higher amount of Sn, which are absent in our undoped nanowires and appear less intense in the sample with less amount of Sn. This indicates that the observed infrared emission is related to Sn, possibly by the introduction of defect states. Wang *et al* [20] have recently reported on 1 and 1.4 eV photoluminescence bands which increase on oxidation of Ge nanocrystals and are attributed to the presence of deep levels in the interface between the oxide and the Ge nanocrystals. The infrared bands observed in this work are, however, associated to doped GeO_2 and not to Ge. Waveguide behavior of the doped nanowires with cross-section down to 600 nm has been observed for red and green laser light (figure 7), which confirms the potential application of these nanostructures in optical nanodevices.

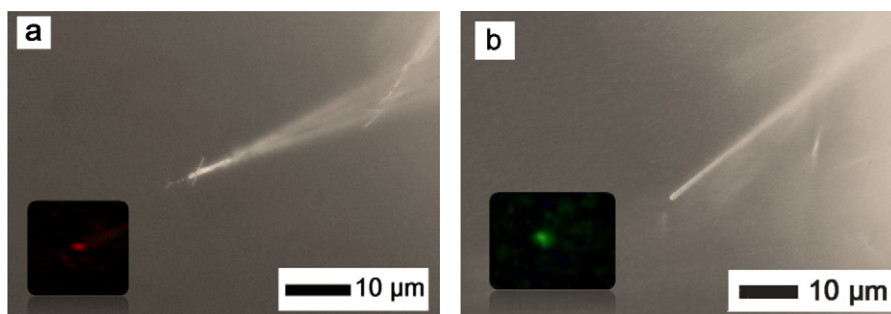


Figure 7. Optical images of the end of two long straight wires. In (a) the inset shows the red spot and in (b) the inset shows the green spot observed at the end of the wires due to the waveguiding behavior during the corresponding illumination.

(This figure is in colour only in the electronic version)

4. Conclusions

Thermal treatment of a compacted mixture of Ge and SnO₂ powders, with small SnO₂ content, leads to the growth of Sn doped GeO₂ nanowires on the sample surface. The presence of Sn prevents the formation of sharp bends and reduces the cross-sectional dimension of the wires as compared with undoped wires grown by the same method. The morphology of the Sn doped nanowires appears then to be more favorable for their use as nanosize waveguides. Sn doping does not modify the visible cathodoluminescence of the nanowires but introduces levels related to several luminescence bands in the near-infrared range. Waveguiding behavior of the Sn doped GeO₂ for red and green laser light was demonstrated.

Acknowledgment

This work was supported by MEC (Project MAT2006-01259).

References

- [1] Hidalgo P, Méndez B and Piqueras J 2007 *Nanotechnology* **18** 155203
- [2] Bai Z G, Yu D P, Zhang H Z, Ding Y, Wang Y P, Gai X Z, Hang Q L, Xiong G C and Feng S G 1999 *Chem. Phys. Lett.* **303** 311
- [3] Tang Y H, Zhang Y F, Wang N, Bello I, Lee C S and Lee S T 1999 *Appl. Phys. Lett.* **74** 3824
- [4] Dang H Y, Wang J and Fan S S 2003 *Nanotechnology* **14** 738
- [5] Hidalgo P, Méndez B and Piqueras J 2005 *Nanotechnology* **16** 2521
- [6] Nogales E, Méndez B and Piqueras J 2005 *Appl. Phys. Lett.* **86** 113112
- [7] Grym J, Fernández P and Piqueras J 2005 *Nanotechnology* **16** 931
- [8] Magdas D A, Cremades A and Piqueras J 2006 *Appl. Phys. Lett.* **88** 113107
- [9] Díaz-Guerra C and Piqueras J 2007 *J. Appl. Phys.* **102** 084307
- [10] Li S Y, Lin P, Lee C Y, Tseng T Y and Huang C J 2004 *J. Phys. D: Appl. Phys.* **37** 2274
- [11] Wang Q, Song Z T, Feng S L and Wang T H 2004 *Appl. Phys. Lett.* **85** 4759
- [12] Li S Y, Lee C Y, Lin P and Tseng T Y 2005 *Nanotechnology* **16** 451
- [13] Ortega Y, Fernández P and Piqueras J 2007 *Nanotechnology* **18** 115606
- [14] Wu J and Coffey J L 2007 *Chem. Mater.* **19** 6266
- [15] Li S Y, Lin P, Lee C Y, Tseng T Y and Huang C J 2004 *J. Phys. D: Appl. Phys.* **37** 2274
- [16] Wen J G, Lao J Y, Wang D Z, Kyaw T M, Foo Y L and Ren Z F 2003 *Chem. Phys. Lett.* **372** 717
- [17] Lao J Y, Wen J G and Ren Z F 2002 *Nano Lett.* **2** 1287
- [18] Lao J Y, Huang J Y, Wang D Z and Ren Z F 2004 *J. Mater. Chem.* **14** 770
- [19] Gao P X and Wang Z L 2004 *Appl. Phys. Lett.* **84** 2883
- [20] Wang W, Wang K, Han D, Poudel B, Wang X, Wang D Z, Zeng B and Ren Z F 2007 *Nanotechnology* **18** 075707