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# High aspect ratio GeO<sub>2</sub> nano- and microwires with waveguiding behaviour

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## Abstract

High aspect ratio GeO<sub>2</sub> nano- and microwires have been grown by thermal treatment at 600 °C of compacted Ge powder under argon flow. The wires have cross-sectional dimensions from less than 100 nm to about 1 μm, depending on the duration of the treatment, and lengths of up to about 2000 μm. Waveguide behaviour of the wires was demonstrated for visible light, which shows the potential applications of these structures for optical nanodevices.

## 1. Introduction

Germanium dioxide, GeO<sub>2</sub>, is a blue-green luminescent material with optical properties which are considered of interest for optoelectronic communications, so the fabrication of GeO<sub>2</sub> nanowires would be useful to future optical nanodevices. GeO<sub>2</sub> elongated structures have been prepared by Ge evaporation [1], carbon nanotube confined reaction of Ge [2], electrospinning [3], laser ablation [4], thermal oxidation [5, 6], carbothermal reduction [7] or thermal deposition [8]. The reported GeO<sub>2</sub> nanowires and whiskers often form a dense distribution, sometimes with a network structure, of wires with different aspect ratios. For some applications, as for instance optical waveguides, the growth of isolated wires which do not belong to a network, with high aspect ratio, would be of interest. In the present work, GeO<sub>2</sub> nano- and submicron wires have been grown by thermal treatment of compacted Ge powder under argon flow. This method, growth of elongated nanostructures on the surface of a pellet of compacted powder, during thermal treatment under gas flow, has been previously applied to the case of different oxides [8–12]. In [8], we have grown GeO<sub>2</sub> nanowires and nanoneedles by using GeO<sub>2</sub> powder as the starting material. The present work shows that the use of Ge powder as a precursor to grow GeO<sub>2</sub> nanowires prevents, or retards, the formation of networks which leads to the growth of long straight wires of the oxide with higher aspect ratio. The nanowires have been characterized by x-ray diffraction, scanning electron microscopy (SEM), cathodoluminescence (CL) in SEM and transmission electron microscopy (TEM). The waveguide behaviour of the wires has been investigated by illumination with light of different wavelengths.

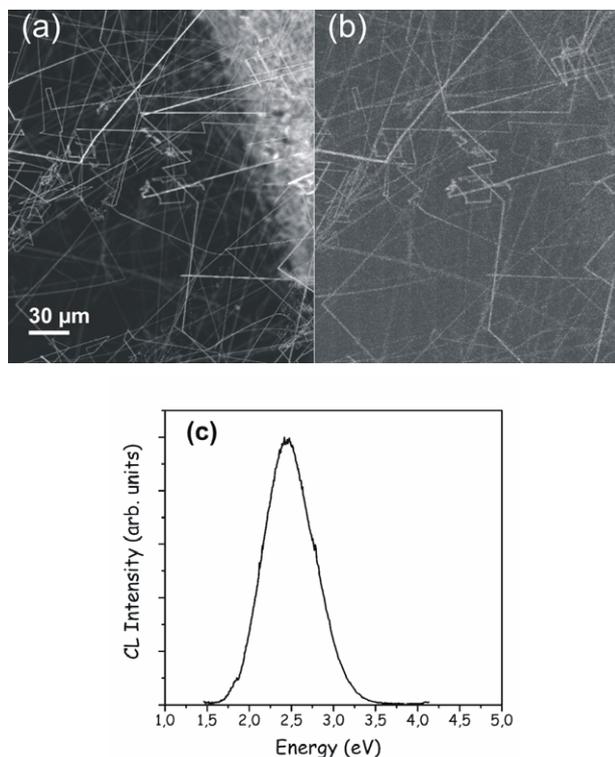
## 2. Experimental method

Ge powder with 99.999% purity was used as starting material. Samples were prepared by compacting the powder under a compressive load to form discs of about 7 mm diameter and 2 mm thickness. The range of the grain size is between 2 and 10 μm. A series of discs were then annealed under Ar flow at 600 °C for times between 1 and 15 h. The furnace was not sealed for vacuum conditions so that air leaking into the furnace acts as a source of oxygen.

XRD measurements were performed in a Philips diffractometer. Secondary electron 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 and a Hamamatsu PMA-11 charge coupled device camera. TEM observations were performed with a JEOL JEM 2000 FX microscope. For the waveguide measurements with an optical microscope, nano- and microwires were glued at the end of a commercial light guide of 100 μm diameter, which guided 640 nm or 535 nm laser light or light from a blue LED with peak emission at 475 nm.

## 3. Results and discussion

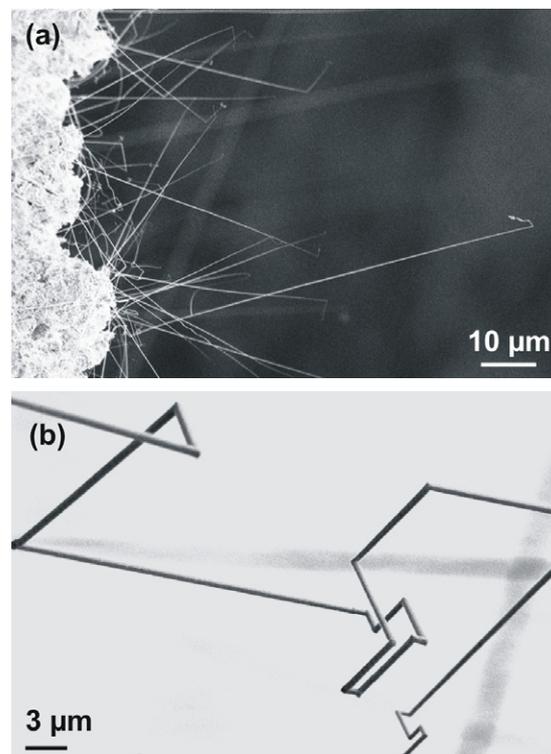
In all samples investigated, the thermal treatments cause the growth of nanowires whose dimensions depend on the specific treatment as described below. XRD of the wires shows the (101) peak of the hexagonal α-GeO<sub>2</sub> structure, as the only main peak in the spectrum, while no Ge peak was observed. CL images in the visible range showed an intense emission from



**Figure 1.** (a) Secondary electron image of  $\text{GeO}_2$  wires. The right part of the image corresponds to the disc made of compacted Ge powder, which acts as substrate for the growth of wires. (b) CL image showing the wire distribution while the non-luminescent substrate is not observed. (c) CL spectrum of  $\text{GeO}_2$  nanowires.

the nanowires, while in the disc background, no, or very weak, luminescence was observed (figure 1). The CL spectrum of the nanowires with a band peaked at about 2.44 eV is shown in figure 1(c). The spectral shape is independent of the duration of treatment. Also, CL spectra of discs prepared with  $\text{GeO}_2$  powder and annealed under the same conditions as the samples with nanowires have the same shape. This confirms that the nanowires are of  $\text{GeO}_2$ . The spectrum shown in figure 1 is similar to the CL spectra of  $\text{GeO}_2$  nanowires grown from  $\text{GeO}_2$  powder, reported in [8], and its main features agree with previous  $\text{GeO}_2$  luminescence observations from other authors, as discussed in [8].

In the sample treated at 600 °C for 1 h, straight nanowires with diameters between 80 and 200 nm and lengths of several tens of microns are observed (figure 2(a)). Some wires of this sample have a length to diameter aspect ratio of about 400. Formation of junctions of intersecting nanowires, by sintering, interpenetration or other mechanism, is not, or only occasionally, observed. Sintering of nanowires has been found in other materials to lead to the formation of networks [13–15] which limits the length of the growing nanowires or nanorods. In this sample, wires crossing at close distances show clearly separated paths. The abrupt change of growth direction, which is apparent in some of the wires of figure 2(a), is more clearly observed in the samples treated for longer time, as figure 2(b), which corresponds to a sample treated for 15 h, shows. In general the SEM images suggest that the growth front of a single wire does not interact with the lateral faces of other

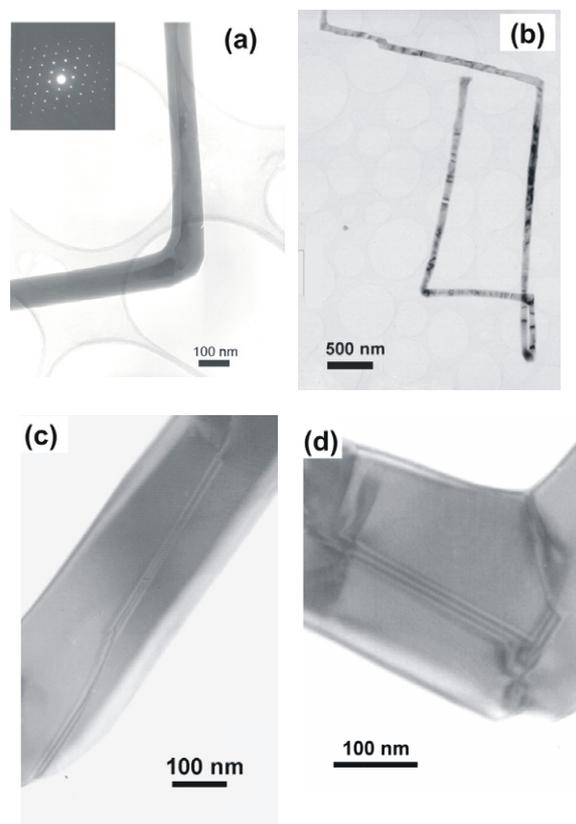


**Figure 2.** SEM images from wires at different stages: (a) in the first stage of growth most of the wires follow a straight line while only incipient bends are observed; (b) in advanced stages of growth, the wires are formed by segments which form well defined angles, suggesting a crystallography-based mechanism.

wires, avoiding the formation of networks or interconnected arrays. A direction change of a single wire appears to be more favourable than the formation of a junction. SEM images (e.g. figure 2) indicate that the sharp changes in the growth direction of the wires occur in almost every long wire and not occasionally. The bending does not take place at random but at preferential angles, suggesting a crystallography related mechanism.

By increasing the annealing time, both, length and cross-sectional dimensions of the wires increase. However, the cross-sectional dimensions appear to saturate, in the range of annealing times used, while the length clearly increases with annealing time, which leads to the growth of wires with high aspect ratio. In particular, the wires obtained after the 15 h treatment show a four-sided cross section with dimensions in the range 700–800 nm, and lengths that reach the millimetre range, so that many wires have aspect ratios in the range 1000–2000 or higher. Tang *et al* [4] produced germanium dioxide whiskers of the hexagonal  $\alpha$ -phase, of 2  $\mu\text{m}$  average diameters, with morphologies corresponding to hexagonal, triangular and quadrilateral cross sections, and described how such morphologies can appear in  $\alpha$ -phase hexagonal crystals. This agrees with the quadrilateral cross section observed in our larger wires.

Figure 3(a) shows the TEM image of a nanowire in a bend region. Diffraction patterns were recorded at the bend and at close regions at both sides. The three patterns correspond to the (011) zone axis of the hexagonal structure and show that



**Figure 3.** TEM images of the nanowires. (a) Bend region of a nanowire. The inset shows the electron diffraction pattern. Diffraction patterns at both sides of the bend and in the bend region correspond to the (011) zone axis of the hexagonal structure. (b) Nanowire with planar defects perpendicular to the growth axis. (c) Nanowire with a twin along the growth direction. (d) Twin in a bend region.

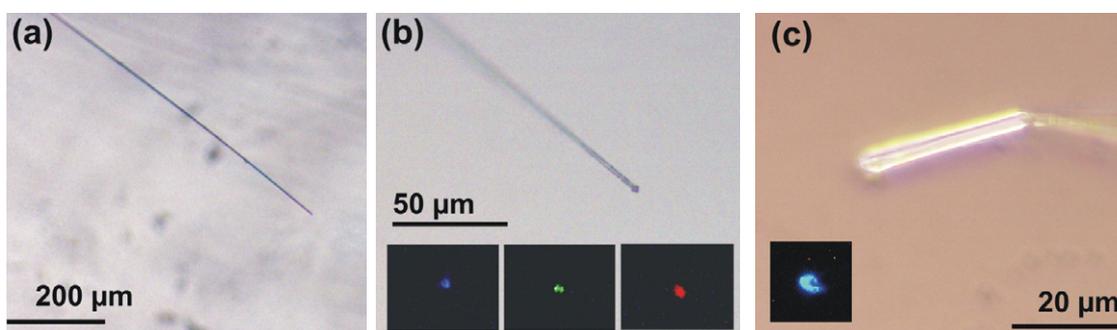
the selected areas are single crystalline (figure 3). Comparison of the diffraction patterns shows that the bend region is tilted about  $1^\circ$  relative to the merging wire segments. Series of planar defects, perpendicular to the growth axis are found in some of the nanowires (figure 3(b)) and in some wires with larger correction, a twin boundary parallel to the growth axis is observed (figure 3(c)) showing the growth of bicrystalline  $\text{GeO}_2$  nanowires. The presence of twins may favour the

growth of the  $\text{GeO}_2$  nanowire parallel to the twin plane. A similar behaviour has been reported for bicrystalline  $\text{ZnO}$  [16] suggesting that the twin structure plays a key role to lead an axial growth. A change of the twin plane would involve the bend of nanowire in the same way, as figure 3(d) shows. Since  $\text{GeO}_2$  becomes amorphous under a high energy electron beam, more detailed TEM observations could not be performed.

Waveguiding was observed for red, green and blue light in wires with cross-sectional dimensions of about 700 nm or larger, and lengths of up to about 2 mm. The behaviour of thinner nanowires could not be investigated with our experimental system. Waveguides of crystalline oxide nanowires have been previously reported for  $\text{SnO}_2$  [17]. The fact that  $\text{GeO}_2$  is luminescent in the blue-green range does not appear to prevent the waveguide behaviour. In fact, blue light, which could be absorbed during its path in the wire and excite blue-green luminescence, was clearly detected at the exit spot of the wire. Figure 4 shows one wire with length over  $800 \mu\text{m}$ , and the blue, green and red spots at its end, recorded under the corresponding illumination. In the wires with abrupt direction changes, light propagation is also observed, even in fibres containing several  $90^\circ$  direction changes in their path, although in such cases, some light loss is observed at the bend. Figure 4(c) shows the image of a fibre with a sharp bend and the light spot observed at the end.

#### 4. Conclusions

In summary, thermal treatment of Ge compacted powder at  $600^\circ\text{C}$  under argon flow leads to the formation of  $\text{GeO}_2$  nano- and microwires formed by straight segments and aspect ratios up to about 2000. During the growth, no wire networks are formed and wire junctions are only occasionally observed, which indicates that the contact of the growth front of a nanowire with other nanowires is not energetically favourable. Twins and bicrystalline nanowires are observed. The nanowires show an intense luminescence emission band centred at 2.44 eV. Waveguide behaviour of wires with cross-sectional dimensions of about 700 nm and lengths up to  $2000 \mu\text{m}$  has been demonstrated for red, green and blue light even for wires with a number of  $90^\circ$  bends.



**Figure 4.** (a) Optical image of a long straight wire. (b) Detail of one of the ends of the fibre shown in (a). The inset shows the blue, green and red spots observed at the end of the wire due to the waveguiding behaviour during the corresponding illumination. The magnification bar of the figure does not apply to the spots. (c) Detail of a wire showing a  $90^\circ$  bend and the blue spot observed at the end of the fibre when the wire acts as a waveguide.

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