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GeO_2 nanowires and nanoneedles grown by thermal deposition without a catalyst

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Abstract
Thermal treatment of compacted GeO_2 powder under argon flow leads to the growth of a dense distribution of microwires and nanowires on the sample surface. Extended treatment causes the formation of more complex structures, including arrays of nanoneedles. Enhanced cathodoluminescence emission is associated with the wires and needles, which show a component at 2.72 eV not observed for the untreated material.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Elongated semiconductor nanostructures are being increasingly investigated due to their potential use in future nanoelectronic and optical nanodevices. Nanowires, nanotubes and nanoneedles have been fabricated by different methods and, in particular, thermal deposition methods, with and without the use of a catalyst, have been frequently applied. A high activity in this field is related to the fabrication of elongated nanostructures of oxides, such as ZnO, SnO_2 and Ga_2O_3. Germanium dioxide, GeO_2, is a blue luminescent material with optical properties which are considered of interest for opto-electronic communications, so the fabrication of GeO_2 nanowires would be useful to future optical nanodevices. GeO_2 nanowires have been prepared by Ge evaporation [1], carbon nanotube confined reaction of Ge [2], electrospinning [3], laser ablation [4], thermal oxidation [5, 6] and carbothermal reduction [7]. In the above-mentioned works, mainly structural characterization has been performed, while the emission properties of the nanostructures have not in general been investigated. On the other hand, luminescence properties of nanocrystallites of germanium oxide either embedded in an oxide matrix [8] or obtained by ball milling [9] have been reported.

In the present work, GeO_2 nanowires and nanoneedles have been grown by a thermal treatment of compressed germanium oxide powder, under an argon flow. This method has been previously reported to lead to the growth of elongated microstructures and nanostructures of different semiconductor oxides [10–12] and of CdSe [13]. The GeO_2 nanostructures obtained have been characterized by scanning electron microscopy (SEM) and using cathodoluminescence (CL) in SEM.

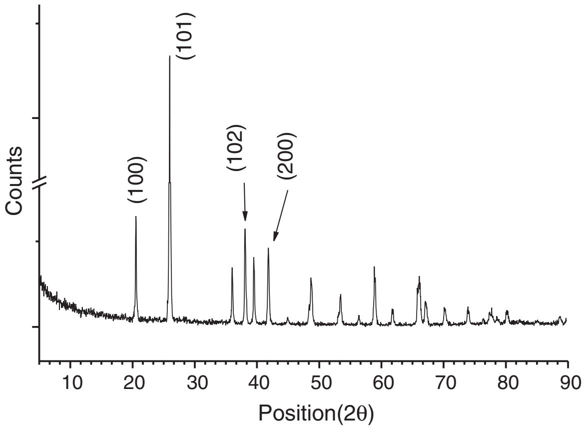

Figure 1. XRD spectrum of thermally treated GeO_2, showing hexagonal α-GeO_2 structure.

2. Experimental method

The starting material was GeO_2 powder with a purity of 99.9999%. Samples were prepared by compacting the powder under a compressive load to form discs of about 7 mm diameter and 2 mm thickness. The discs were then annealed under Ar flow at 1100 °C for times between 24 and 28 h; however, no marked differences were observed after either treatments. The resulting samples were characterized by means of x-ray diffraction (XRD) to assess their crystalline structure. SEM measurements were performed either in a Leica 440 or a Hitachi S-2500 scanning electron microscope. The CL measurements were carried out at liquid nitrogen temperature by using a Hamamatsu R-943 photomultiplier at 15 keV electron beam energy.

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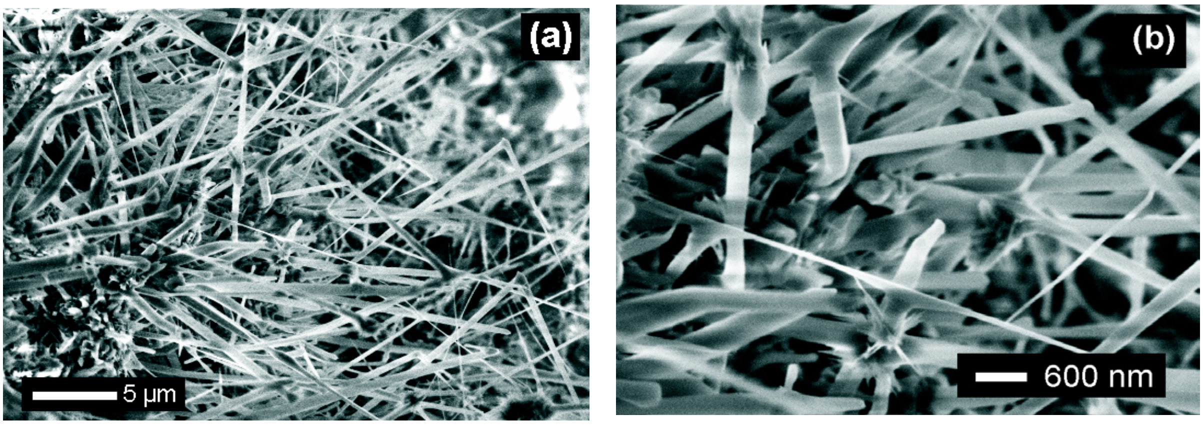

Figure 2. SEM images of the GeO_2 nanowires grown at 1100 °C at low (a) and high (b) magnification.

3. Results and discussion

The XRD by the treated samples (figure 1) shows the hexagonal α-GeO_2 structure. The thermal treatment leads to a rough surface, in which clusters of grains separated by empty spaces, forming a poorly compacted sample, are observed. Most of the surface of the thermally treated samples appear covered with elongated microstructures and nanostructures. The structures grown on the sample surface are microwires and nanowires, nanoneedles, as well as cactus-like structures with nanoneedles distributed as cactus spines. Figure 2(a) shows an area covered with nanowires in the sample annealed for 24 h. Figure 2(b), showing the same area at higher magnification, shows that many of the wires exhibit widths in the range of 100–500 nm. The lengths of the wires extend to several micrometres. SEM images show that the different morphologies appear to correspond to different stages of growth. In particular, the presence of dense arrays of wires, as in figure 2, corresponds to a first stage, while the cacti appear during a later stage, in regions with a high density of nanostructures and also at the rim of the sample, which is a preferential nucleation site. Figure 3(a) shows a cactus-like structure, figure 3(b) shows a region of the rim of the disc where well developed cacti are the dominant structures and figure 3(c) shows a cactus in a preliminary formation stage. The formation of wires was first observed after 20 h of treatment. For 24 h treatment SEM images show initial stages of cactus structure and a high density of wires, while for 28 h treatment the oriented needles appear, forming denser arrays. A higher magnification image (figure 4) shows that the cacti are covered with arrays of nanoneedles oriented along two well defined directions, forming an angle of about 60°, which suggests that the needles are oriented along the crystallographic $\langle 100\rangle$ and $\langle 110\rangle$ directions, whose angle in the GeO_2 structure is 63°. Thermal evaporation of powder under gas flow and deposition on a substrate is an often reported method for growing elongated semiconductor nanostructures. In many cases a catalyst, such as gold, is necessary for the growth by means of a vapour–liquid–solid (VLS) process [14, 15]. In our case the source is a disc of material which is also the substrate for the nanostructures obtained without the use of a catalyst, indicating the existence of a vapour–solid process.

The growth of the nanostructures causes enhancement of the luminescence intensity, as shown in figure 5 in which higher CL emission arises from wires and cactus-like formations in a nanostructure-rich region of the sample. CL spectra

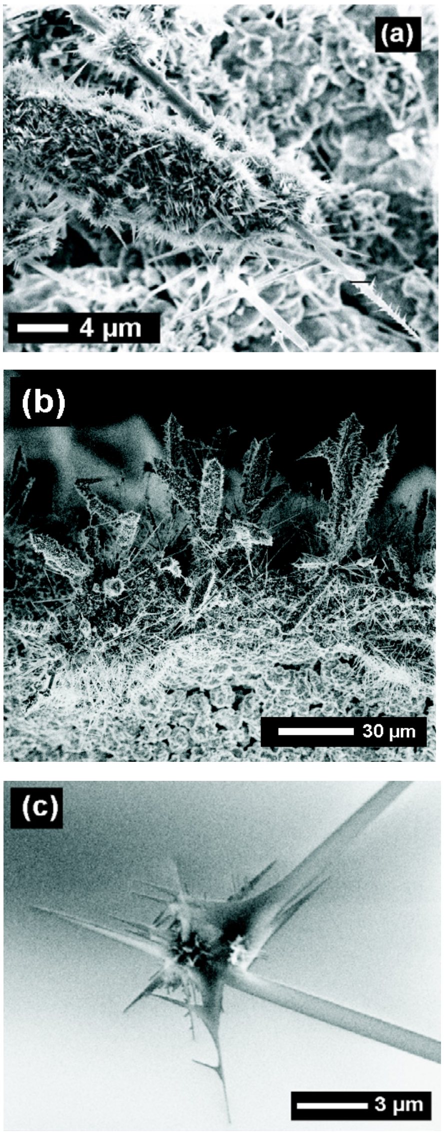

Figure 3. (a) SEM image of a cactus-like formation, (b) SEM image from the rim of the sample and (c) detail of the initial stages of the formation of this structure.

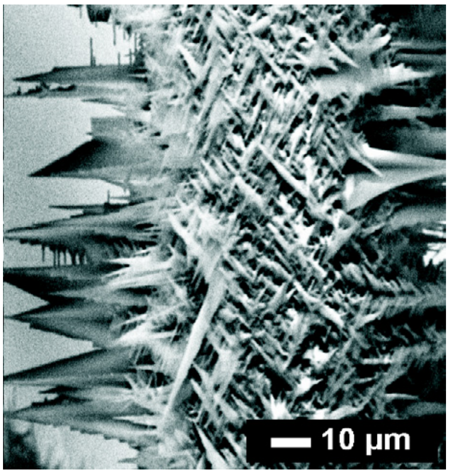

Figure 4. SEM image of the array of nanoneedles, which form the cactus, oriented along ⟨110⟩ and ⟨100⟩ directions.

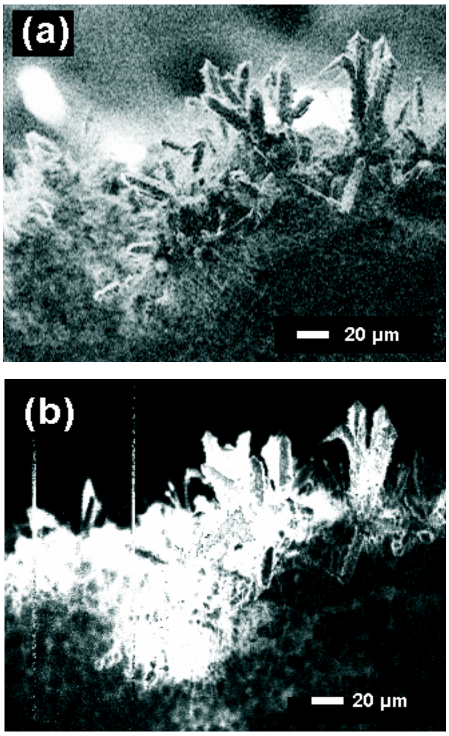

Figure 5. Secondary-electron (a) and cathodoluminescence (b) images of the formations grown on the GeO_2 surface.

of the samples before the thermal treatment—dotted line in figure 6(a)—show a blue-green band with the main peak at 2.40 eV. Local CL spectra of nanostructure-rich areas—solid line in figure 6(a)—are dominated by a complex blue-green band with a main peak centred at 2.44 eV along with a shoulder at higher energies. Gaussian deconvolution of the solid line spectrum shows that the shoulder corresponds to an emission band at 2.72 eV and that the blue-green band has components at 2.25 and 2.44 eV (figure 6(b)). The 2.25 eV component, necessary for a good fit, corresponds to the oxygen vacancy related emission [16].

Visible luminescence from GeO_2 crystals has been previously investigated by means of photoluminescence (PL) and CL and its relationship with the oxygen content and crystalline structure has been discussed. Fitting *et al* [16] found that a green band at 2.25 eV, attributed to the presence of oxygen-deficient centres, dominates the CL spectrum of quartz-like GeO_2 (hexagonal), while for rutile-like GeO_2 (tetragonal), a violet band at 3.1 eV is also present. Zacharias *et al* [8] studied the photoluminescence of GeO_2 nanocrystals embedded in an oxide matrix and suggested that the observed 3.1 eV emission is related to defects in the matrix–nanocrystal interface. CL spectra at 90 K of GeO_2 nanocrystals prepared by mechanical milling [9] show a main band at 2.49 eV and the main emission of GeO_2 commercial powder appears at 2.43 eV. The CL emission from the nanostructures reported here is similar to that of the nanocrystals reported in [9] and shows a slight blue shift relative to the starting powder as well as the component at 2.72 eV. The cause of the slight shift of the main peak relative to the starting powder (from 2.40 to 2.44 eV) could be related to the presence of different defects, as a consequence of the thermal treatment, but it cannot be determined from the present results.

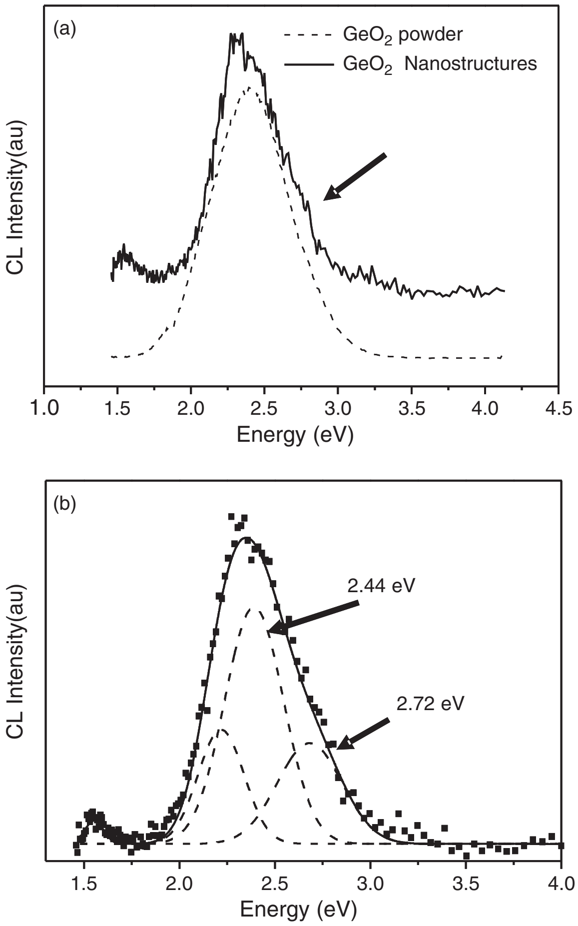

Figure 6. (a) Local CL spectrum from the nanowires and nanoneedles of GeO_2 (solid line) and of the starting powder (dashed line). (b) Deconvoluted CL spectrum of the nanostructure-rich area showing the main blue-green emission and the component at 2.72 eV.

4. Conclusions

In summary, thermal treatment of GeO_2 compacted powder at 1100 °C under argon flow leads to the formation of microwires and nanowires on the sample surface. For longer treatments more complex arrangements including nanoneedles and cactus-like microstructures are formed. Nanowires, nanoneedles and the complex structures containing them show enhanced CL emission and a slight spectral blue shift as compared with the starting material.

Acknowledgments

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