

GeO₂ nanotubes and nanorods synthesized by vapor phase reactions

Z. Jiang*, T. Xie, G.Z. Wang, X.Y. Yuan, C.H. Ye, W.P. Cai, G.W. Meng, G.H. Li, L.D. Zhang

Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

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Abstract

Bulk-quantity GeO₂ nanorods and nanotubes have been synthesized by simple thermal evaporation of metallic germanium powders. The nanorods and nanotubes have a diameter of about 100–150 nm and length of about 1 μm. Many of the nanotubes have a serrated out surface which is formed by twin crystals. The twin boundary can strengthen the mechanical property and increase the electrical resistance and thus vary the physical property of GeO₂. The products can emit bright blue light with a peak at 448 nm under excitation at 381 nm at room temperature. So the products may have potential application in future integrated optical devices.

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1. Introduction

Nanoscale one-dimensional (1D) materials (such as nanowires, nanotubes, nanobelts, etc.) have attracted much attention due to their remarkable physical, chemical and mechanical properties [1–4]. Germanium oxide (GeO₂) is an important material for optical fibers, which has a blue luminescence [5] with peak energies around 3.1 eV (400 nm) and 2.2 eV (563.6 nm). GeO₂-based glass is thought to be more refractive and has higher linear coefficient of thermal expansion than the corresponding of SiO₂ [6]. Another important application of GeO₂ is in the vacuum technology [7]. Several synthesis methods of 1D structures of GeO₂ have been reported, such as GeO₂ whiskers synthesized by laser ablation [8], GeO₂ nanowires prepared via physical evaporation [9] and carbothermal reaction [6], dot-patterned nanowires of α-GeO₂ prepared by the oxide-assisted growth method [10] and GeO₂ nanorods grown by carbon nanotube confined reaction [11]. As the nanotubes are superior to other morphologies as both inner and outer surfaces can be modified, and up to now, there are rarely reports about GeO₂ nanotubes. So in this communication,

we report the preparation of GeO₂ nanotubes and nanorods by a simple chemical evaporation method. The as-synthesized nanostructures of GeO₂ may have potential applications in nanodevice with diverse functions.

2. Experimental procedure

The synthesis of GeO₂ nanotubes and nanorods was carried out in a simple CVD system composed of a high-temperature horizontal tube furnace and a digital gas flow controller. The raw materials used in this work were Ge powders (mass purity: 99.999%). A boat containing 2 g metallic Ge powders was placed in the center of furnace. The cleaned polished Al₂O₃ (0001) wafers were placed in another alumina boat which was transferred into the alumina tube at the downstream side. The system was flushed with high-purity argon (purity 99.99%) for 1 h to eliminate O₂, then rapidly heated to 1100 °C and kept at the temperature for 2 h. During the experiment, the constant gas flow with high-purity Ar (50 sccm) and hydrogen (10 sccm) was maintained. When the system was cooled to room temperature, a large area of white products was found on the Al₂O₃ wafers and the inner wall of alumina boat. The structure of white product was characterized and analyzed by X-ray diffraction (XRD) [D/MAX-γB with Co radiation (λ=0.178897 nm)], transmission

* Corresponding author. Tel.: +86 5515591476; fax: +86 5515591434.
E-mail address: zjiang@issp.ac.cn (Z. Jiang).

electron microscopy (TEM) (Hitachi Model H-800), and high-resolution transmission electron microscopy (HRTEM) (JEOL-2010) with an energy-disperse spectroscopy (EDS) (EDAX DX-4). The photoluminescence (PL) spectrum was obtained using an Edinburgh FLS 920 fluorescence spectrophotometer (Xe 900 lamp) under excitation at 381 nm at room temperature.

3. Results and discussion

After ultrasonic dispersion in alcohol, the sample was put onto a transmission electron microscopy (TEM) grid for structural analysis. It was found that the products have a rod-like morphology with diameter distribution from 100 to 150 nm and length ranging from 550 to 1000 nm (Fig. 1a). The selected area electron diffraction (SAED) (top inset in Fig. 1a) pattern shows the products' single crystal properties. The energy-disperse spectroscopy (EDS) which is detected from several rod-like products indicated that they only contained two elements: Ge and O. The structure of the products was characterized by XRD (Fig. 1b). All peaks can be determined as hexagonal GeO_2 crystal (JCPDS No. 85-1519) according to the peak positions and their relative intensities. Further observation of TEM shows that these rod-like products consist of nanotubes and nanorods (Fig. 2). The amount of GeO_2 nanotubes in the total products is about 10%. Some of them have partially hollow core. In the process of investigation by TEM, the rod-like products are found to be very sensitive to the irradiation of the electron beam. This phenomenon has been described in the previous papers [8,11].

A comprehensive TEM investigation reveals that in our experiment, many of the nanotubes have a serrated outer surface. Fig. 3a is a typical high-resolution transmission electron microscope (HRTEM) image of GeO_2 nanotube. The image shows that the nanotube has two open ends with a smooth inner wall and a serrated outer surface. This interesting morphology is not the same as that of the previous reported nanotubes with smooth surface (such as Refs. [12–14] and others). The nanotube has inner diameter of about 50 nm and average outer diameter of 100 nm and length up to 500 nm. The diffuse reflection of SAED pattern

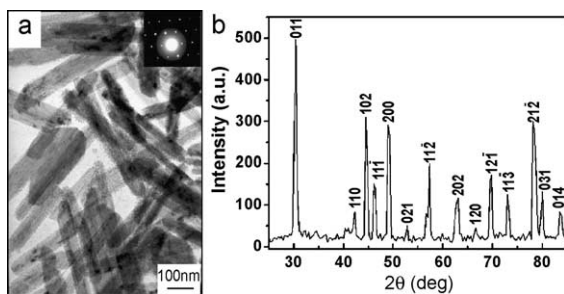


Fig. 1. (a) TEM image of GeO_2 rod-like products; SAED pattern (top inset) shows the crystalline property. (b) XRD pattern recorded from the GeO_2 nanorods and nanotubes.

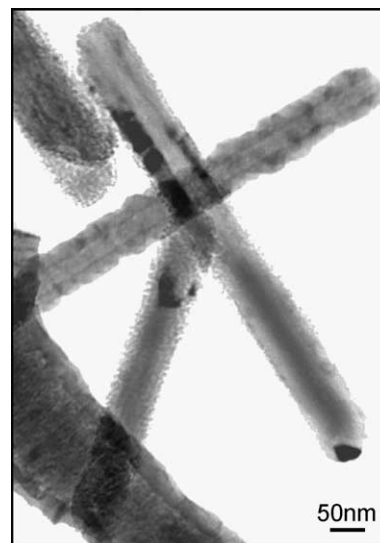


Fig. 2. The enlargement TEM image of GeO_2 nanotubes and nanorods; the image also shows a nanorod with a partially hollow core.

(top inset in Fig. 3a) indicates that the nanotube contains many stacking faults and twin crystals. This phenomenon is also confirmed by the HRTEM image. The HRTEM image reveals clearly that these serrated surface nanotubes contain many parallel twin boundaries (T.B) and stacking faults (Fig. 3b) and the twinned crystals have larger cross section than the tube, which formed the serrated outer surface of the nanotube (Fig. 3b). The image also shows that the serrated outer surface is covered with a thin amorphous surface layer. The crystal interlayer distance is ca. 0.426 nm which agrees well with the separation between (100) planes of hexagonal GeO_2 (JCPDS No. 85-1519, $d_{100}=0.42519$ nm).

It is well known that the twin boundary (T.B), a special kind coherent boundary, not only increases the scattering of conducting of electrons, but also blocks the dislocation motion. Thus they can strengthen the mechanical property and increase the electrical resistance of GeO_2 . These phenomena will cause the as-synthesis products to have different physical properties from the previous reports [6,8–

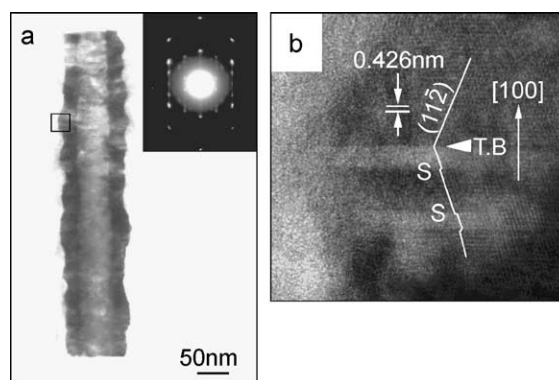


Fig. 3. (a) The special TEM image of GeO_2 nanotube with two open ends has serrated outer wall. (b) The HRTEM image of serrated outer wall reveals that the serrated edges are formed by twin crystals. T.B means twin boundary, and S means stacking faults.

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