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Self Catalyst Germanium Dioxide Comets-Like Nanowires by Thermal Evaporation

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Abstract: GeO_2 Comets -like nanowires structure have been fabricated by simple thermal evaporation method, using Ge powder as the starting material and Si substrate as a collector, at a temperature about 1150°C. The Transmission Electron Microscopy (TEM) of the product showed diameters of nanorods/nanowires about 50-200 nm and length of about 2-40 μm. Strong photoluminescence peak at around 400 nm (~3.1 eV) observed and suggested that it is related to blue emission light.

Key words: Ge, GeO_2, nanowires, self-catalytic VLS growth

INTRODUCTION

In recent years, there has been increasing interest in the synthesis of various one-dimensional (1D) nanostructures, such as nanotubes (Charlier *et al*., 1997), nanowires (Morales and Lieber, 1998) and nanoribbons (Pan *et al*., 2001). Their unique geometries and novel properties make them ideal candidates for potential applications in nanoelectronics (Zimmler *et al*., 2008), light emission (Huang *et al*., 2005), energy conversion (Hochbaum *et al*., 2008) and chemical and biomedical sensors (Cui *et al*., 2001). Extensive efforts have been devoted to synthesize 1D nanomaterials with structures and morphologies (Mazeina *et al*., 2009; Liu *et al*., 2009). A clear understanding of the nanostructure formation mechanism is required in order to grow nanowires and nanoribbons with desired morphology or to design more complex structures such as branched (Milliron *et al*., 2004) and hierarchical nanostructures (Cao *et al*., 2008). The Vapor-Liquid-Solid (VLS) mechanism has been most widely used for the growth of nanowires since it offers excellent control of the nanowire growth parameters (Wanger and Ellis, 1964). Meanwhile, the Vapor-Solid (VS) mechanism based on a simple evaporation and condensation method is also usually used to explain the growth processes of 1D nanostructures.

Germanium dioxide (GeO_2) is a dielectric oxide that is considered a promising material for a variety of applications. GeO_2 is an important material that exhibits a visible luminescence (Zacharias and Fauchet, 1998) while GeO_2-based glass is known to have a higher refractive index and higher linear coefficient of thermal expansion than those of SiO_2 (Wu *et al*., 2001), suggesting potential applications in future optical wave guides (Yin and Garside, 1982) and nanoconnections in optical devices and systems. Another important application of GeO_2 is in the area of vacuum technology (Margaryan and Piliavin, 1993). One of the most interesting and urgent challenges in the area of materials science is the fabrication of materials with novel morphologies. Since, inorganic materials with different morphologies and sizes can exhibit different properties (Hulliger, 1994), even if comprised of the same elements, it is worthwhile to fabricate new GeO_2 structures with different morphologies.

In the present study, we report on the synthesis of GeO_2 nanowires using thermal evaporation method, which have a long tail just like comets flying around the Sun. However, to the best of our knowledge, no studies on comets-like GeO_2 structures have been reported. These special morphological GeO_2 NWs may be a promising material in the application of nanodevices.

MATERIALS AND METHODS

The synthesis of GeO_2 nanowires was carried out in a high-temperature horizontal tube furnace. The 99.9%-pure Ge powders were used as the source material, being placed at the alumina boat in the center of the quartz tube. The Si plate was placed directly at the upper covered the alumina boat, which acted as a substrate for collecting the growth products. The vertical distance between the powders and the substrate was approximately 10 mm. The substrate temperature was set to 1150°C in a flow of nitrogen (N_2) gas. The gas flow rate of N_2 was 15 standard liter per min (slm). The products were collected using a Si (100) substrate with the absence of any metal catalyst.

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After 2 h of typical deposition process, the substrate was cooled down and then removed from the furnace for analysis.

The structural properties of the as-grown products were investigated using X-ray diffractometer (XRD; PANalytical X'Pert PRO diffractometer with Cu Kα radiation), scanning electron microscope (SEM, model JEOL JSM-6460LV with energy dispersive X-ray spectroscopy EDX installed.),transmission electron microscope (TEM, Philips CM12 equipped with analysis Doc.version3.2 image analysis system), the photoluminescence PL spectra of the samples were measured with a He-Cd laser (325 nm) at room temperature.

RESULTS AND DISCUSSION

We have synthesized GeO_2 nanowires (comets-like) nanostructures on the Si substrates as shown in SEM images (Fig. 1a-c). Figure 1a shows that the product is composed of a large number of comet-like objects with long tails. Most samples consist of a short rod (in the edge) and a long tail (in the centre) distributed and grown on the middle of spherical - like particles. Their long tails consist of a great quantity of quasi-aligned thin wires with lengths of 20-40 μm. Figure 1b shows the enlarged image of comet-like samples. It indicates that the short rod has a diameter of ~ 90 nm and a length of ~ 2-3 μm. From the image shown in Fig. 1c. The diameter of the tail-wires decreased gradually with an increase in the distance from the spherical particles. The initial wires near the spherical have the largest diameters, which are about 150-200 nm. The nanowires in the middle part of the tail, as shown in Fig. 1c, have the smallest diameters of 50-100 nm near the tip. As shown in Fig. 1d, EDX verified that the comets-like nanostructures mainly consist of two elements Ge and O, indicating that the product is GeO_2 comets-like nanowires.

Figure 2 shows the XRD spectrum of the product. All recognizable reflection peaks including (100), (101), (110), (102), (111), (200), (201), (112), (202), (211) and (203) can be clearly indexed to the hexagonal structure of GeO_2 with lattice constants of a = 4.987 Å and c = 5.652 Å (JCPDS File No. 04-0497).

The detailed structure of comets-like GeO_2 nanowires was characterized by TEM as shown in Fig. 3. From the TEM image in Fig. 3a, only short four or five

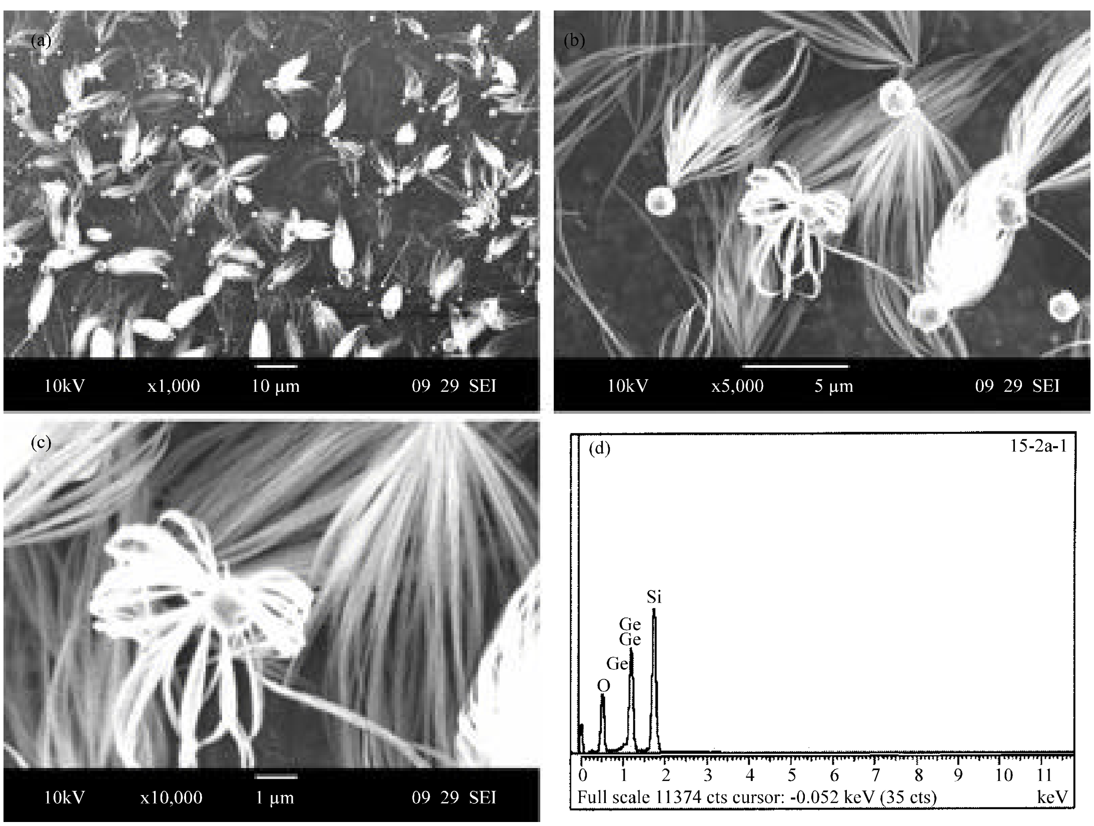

Fig. 1: SEM images of the GeO_2 comets-like nanowires grown at 1150°C at (a) low and (b, c) high magnification, respectively. (d) EDX spectrum revealing that the nanowires spectrum is composed of Ge and O elements

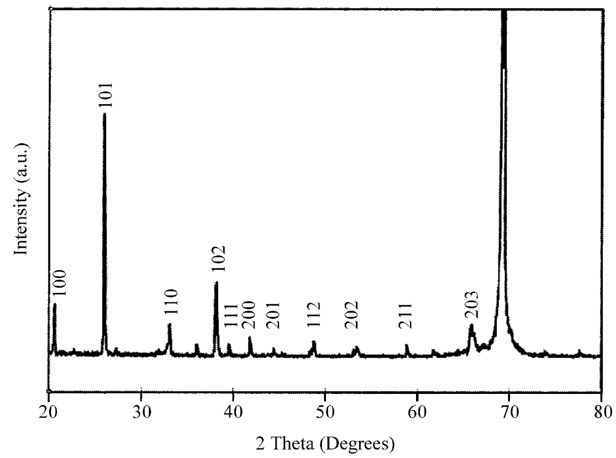

Fig. 2: XRD pattern of the GeO_2 comet-like nanowires

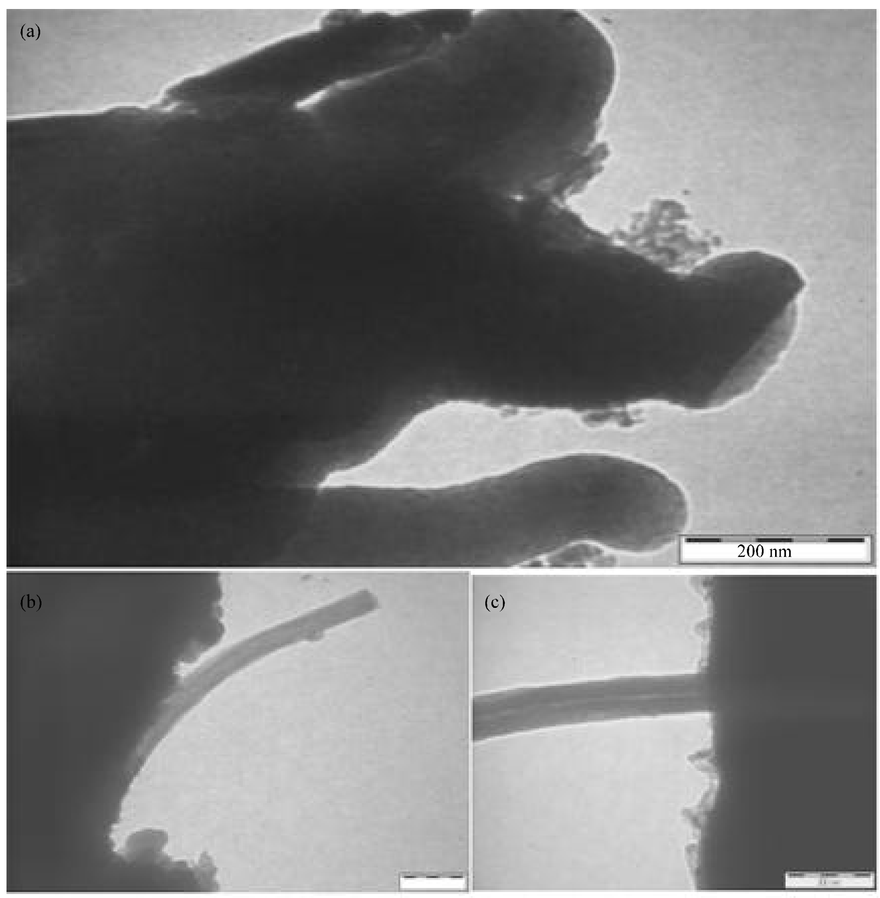

Fig. 3: TEM image showing (a) only short four or five nanorods/nanowires of the GeO_2 structures, (b) Brocken nanowire and (c) middle long nanowire

nanorods/nanowires structure could be observed. This is because the most wires and rods had been broken, while we are doing the ultrasonic process for the sample in aceton solution (Fig. 3b). The TEM picture of Fig. 3a-c clearly showed the average difference of diameters (about 50-200 nm) and length of (about 2-40 μm) the nano-rods/wires.

When synthesis was carried out at high temperature (1150°C) in the present work, the growth mechanism of our GeO_2 comet-like nanostructures should be one of well known, two growth mechanisms exist, i.e., VLS (vapor-liquid-solid) and VS (vapor-solid), to explain the growth of one dimensional nanostructures in such a thermal evaporation process. In the VLS process, a transition metal particle (such as gold, iron, etc.) capped at the tip of the nanowires serves as the catalytic active site, which is almost characteristic of VLS growth (Zhang and Zhang, 2002; Pan *et al.*, 2002; Liang *et al.*, 2001; Jiang *et al.*, 2002). In this experiment, the nanowires grown from the spherical particles (liquid drops of Ge) confirm that these nanowires are formed via a VLS mechanism. Commonly, in the VLS process, Au, Fe etc. were added specially as metal catalyst. But in our experiment, the catalyst Ge was the source material, what's more, the as-grown product is GeO_2 nanowires. This growth mechanism is called Self-catalytic VLS growth (Chen *et al.*, 2003; Liu *et al.*, 2003). The growth process of the GeO_2 nanowire arrays could be divided into five steps: (1) with the increase of the temperature, Ge vapor is formed at high-temperature zone. (2) Because the superheating at 1150°C, Ge is volatilized at this point and resulted in the conversion of black Ge powder to white powder. The white powder is confirmed to be GeO_2 based on powder XRD spectrum. (3) The Ge vapor is driven by flowing gas and deposited on the surface of the Si wafer to form Ge liquid droplets. at the low-temperature zone which will serve as liquid nucleus for VLS growth of GeO_2 nanowires. (4) The Ge vapor is oxidized to form GeO_2 in the oxygen environment that originates from air leakage or residual oxygen in the N_2 flow and inside the chamber when reaching 1150°C and the reaction can be expressed as:

$$Ge\ (g) + O_2\ (g) \rightarrow GeO_2\ (s)$$

$$GeO_2(s) + Ge\ (g) \rightarrow 2GeO\ (g)$$

$$2GeO(g) + O_2(g) \rightarrow 2GeO_2\ (s)$$

Ge liquid droplets will grow larger for adsorbing the formed GeO_2; meanwhile, they likely react with the oxygen to form GeO_2 directly. The GeO_2 will separate out to form GeO_2 crystalline nuclei due to supersaturating. (5) The GeO_2 crystalline nuclei grow up gradually to form GeO_2 nanowires.

Figure 4 shows the PL emission spectrum of the as-synthesized GeO_2 nanowires measured with a He-Cd laser (325 nm) at room temperature. Strong peak at around 400 nm (~3.1 eV) observed and we suggest that it is related to blue emission light (Zacharias and Fauchet, 1998; Wu *et al.*, 2001; Maed, 1995). In the present study, GeO_2 nanowires were synthesized at high temperature (1150°C) and GeO are volatilized at this point, the oxygen vacancies and oxygen-germanium vacancies pairs easily exists in the product. Therefore, the PL peak in our product is mainly attributed to blue region and in agreement with the suggestion of that the blue region emission is originated from radiative recombination (Wu *et al.*, 2001).

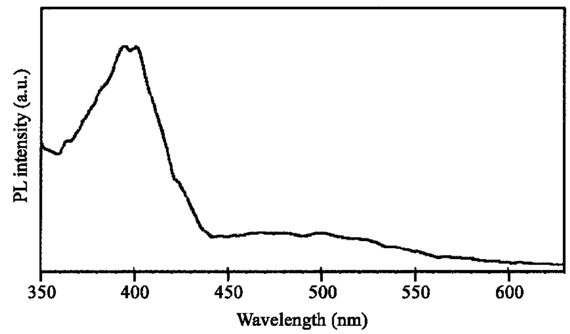

Fig. 4: Photoluminescence spectra of GeO_2 comets-like nanowires

CONCLUSION

Comets -like nanowires structures of GeO_2 have been fabricated by simple thermal evaporation method, using Ge powder as the starting material at a temperature about 1150°C, probably by the VLS process. The products showed the typical hexagonal structure of GeO_2 structure. Strong PL emission peak at around 400 nm (~3.1 eV) observed and we suggest that it is related to blue emission light.

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