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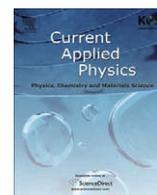
Catalyst-free synthesis of GeO$_2$ nanowires using the thermal heating of Ge powders

Hyoun Woo Kim [*], Jong Woo Lee, Mesfin Abayneh Kebede, Hyo Sung Kim, Chongmu Lee

School of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

ABSTRACT

Germanium dioxide (GeO$_2$) nanowires have been synthesized by means of the simple evaporation of solid Ge powders, without using metal catalysts. The nanowires, with a diameter of about 90–200 nm, were characterized using scanning electron microscopy (SEM), X-ray diffractometry (XRD), and transmission electron microscopy (TEM). The obtained GeO$_2$ nanowires were crystalline with a hexagonal structure. The growth mechanism was discussed with respect to the vapor–solid process. The photoluminescence measurement revealed two emission peaks at about 2.45 eV and 2.91 eV at room temperature, opening up a route to potential applications in future optoelectronic nanodevices. Raman measurement of as-synthesized GeO$_2$ nanowires was made at room temperature.

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1. Introduction

Research in one-dimensional (1D) nanostructures (nanotubes, nanobelts, nanowires, and nanorods) has attracted a great deal of attention because they have promising applications in semiconductor and electronic technologies, particularly for nanoelectronics and optoelectronics [1,2]. Furthermore, the 1D nanostructures are expected to provide an opportunity to understand fundamental concepts about the role of quantum confinement effects. Accordingly, considerable efforts have been made to fabricate some important inorganic materials with their 1D nanostructures [3–5].

Germanium dioxide (GeO$_2$) is a dielectric oxide which can exhibit visible light photoluminescence (PL). Also, it has a refractive index and a linear coefficient of thermal expansion that are higher than those for silicate glass. Accordingly, it is a promising material for optical wave guides [6] and nanoconnections in optical devices and systems.

Up to the present, several synthesis methods of GeO$_2$ 1D structures have been reported, such as laser ablation [7], physical evaporation [8], carbothermal reduction [9], carbon nanotube confined reaction [10], oxide-assisted growth method [11], and electrospinning [12]. However, most studies were carried out by using metal catalyst. In this paper, we have synthesized bulk-quantity GeO$_2$ nanowires by simply heating Ge powders. Not only employing the bare silicon (Si) substrate without metal catalyst will pave the way for integration of future devices with developed Si integrated circuit technology, but also employing conventional powders and simple heating technique will contribute to the future commercialization of the products.

2. Experimental

The synthesis of GeO$_2$ nanowires was carried out in a high-temperature vertical tube furnace. The schematic diagram of the experimental apparatus was previously described [13]. The 99.9%-pure Ge powders were used as the source material, being placed at the lower holder in the center of the quartz tube. The Si plate was placed at the upper holder, which acted as a substrate for collecting the growth products. The vertical distance between the powders and the substrate was approximately 7 mm. The substrate temperature was set to 900 °C in a flow of nitrogen (N$_2$) gas. The gas flow rate of N$_2$ was 20 standard liter per min (slm). The products were collected using a bare-Si(1 0 0) substrate with the absence of any metal catalyst. After 1 h of typical deposition process, the substrate was cooled down and then removed from the furnace for analysis.

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* Corresponding author. Tel.: +82 32 860 7544; fax: +82 32 862 5546.
E-mail address: hwkim@inha.ac.kr (H.W. Kim).

The structural properties of the as-grown products were investigated using glancing angle (0.5°) X-ray diffraction (XRD) with CuKα_1 radiation ($\lambda = 0.154056$ nm), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) with an accelerating voltage of 200 kV, to which energy-dispersive X-ray spectroscopy (EDX) had been attached. For TEM observation, the products were ultrasonically dispersed in acetone and drops were placed on a carbon-coated copper (Cu) grid. PL measurement was conducted at room temperature in a SPEC-1403 photoluminescence spectrometer with the 325 nm line from a He–Cd laser (Kimon, 1K, Japan). Room temperature Raman spectrum was taken with a FT-Raman spectrometer (BRUKER RFS 100/S), equipped with a Nd:YAG laser as a light source operating at a wavelength of 1064 nm.

3. Results and discussion

Fig. 1a shows a typical SEM image, revealing that the product mainly consists of 1D structures. Statistical analysis of many SEM images indicated that the average diameter of the produced 1D structures ranged from 90 to 200 nm. The diameter distribution of the 1D structures is shown in Fig. 1b, revealing that the maximum of diameter distribution occurs in range of 140–160 nm. Fig. 1c shows an enlarged SEM image, indicating that no catalyst particle can be seen at the tip of the 1D structure.

Fig. 2 shows the XRD spectrum of the product. All recognizable reflection peaks including (100), (101), (110), (102), (111), (200), (201), (003), (112), (202), (211), (113), (203), (031), (104), (302), and (114) 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). In the present XRD measurements, the angle of the incident beam to the substrate surface was approximately 0.5° and the detector was rotated to scan the samples, minimizing the contribution from underlayer or substrate.

Fig. 3a shows a TEM image of a single nanowire, revealing that the nanowire has a straight-line morphology. Fig. 3b is a TEM image showing the tip part of a nanowire. It confirms the absence of metal catalyst particle at the tip, agreeing with SEM image (Fig. 1c). The selective area electron diffraction pattern (SAED) of inset corresponds to that of $[\bar{3}31]$ zone axis of the hexagonal GeO$_2$ structure. The spotty pattern reveals the single crystal nature, agreeing with XRD analysis (Fig. 2). Also, a study based on the SAED pattern exhibited the growth direction of this nanowire of [213]. Fig. 3c is an EDX spectrum of the nanowires. There are two peaks visible, which correspond to Ge and O (the Cu peak comes from the Cu TEM grid). Although it is difficult to determine the ratio of the wires quantitatively due to the uncertainty of intensity of the EDX detection for lighter elements, we reveal that the as-synthesized nanowires consist of Ge and O elements.

Among two well-accepted mechanisms for the growth of 1D nanostructures (i.e. vapor–liquid–solid (VLS) and vapor–solid (VS) mechanisms), VLS mechanism is a catalyst-assisted process, in which the metal catalyst particles act as a liquid-forming agent. Since no metal catalyst was used and SEM and TEM images coincidentally indicated that no particle was observed at the ends of the 1D structures in the present work, we surmise that the growth mechanism can be understood on the basis of a self-catalytic process with the characteristics of VS growth mechanism. The growth of the GeO$_2$ 1D nanostructures from the evaporation of Ge powders has been previously reported [14]. It is suggested that Ge powders become oxidized, eventually forming a germanium oxide vapor. The vapor deposits on the surface of the Si substrates, forming nuclei. The nuclei further grow, ultimately forming the GeO$_2$ nanowires. We believe that the oxygen in the GeO$_2$ has been mainly
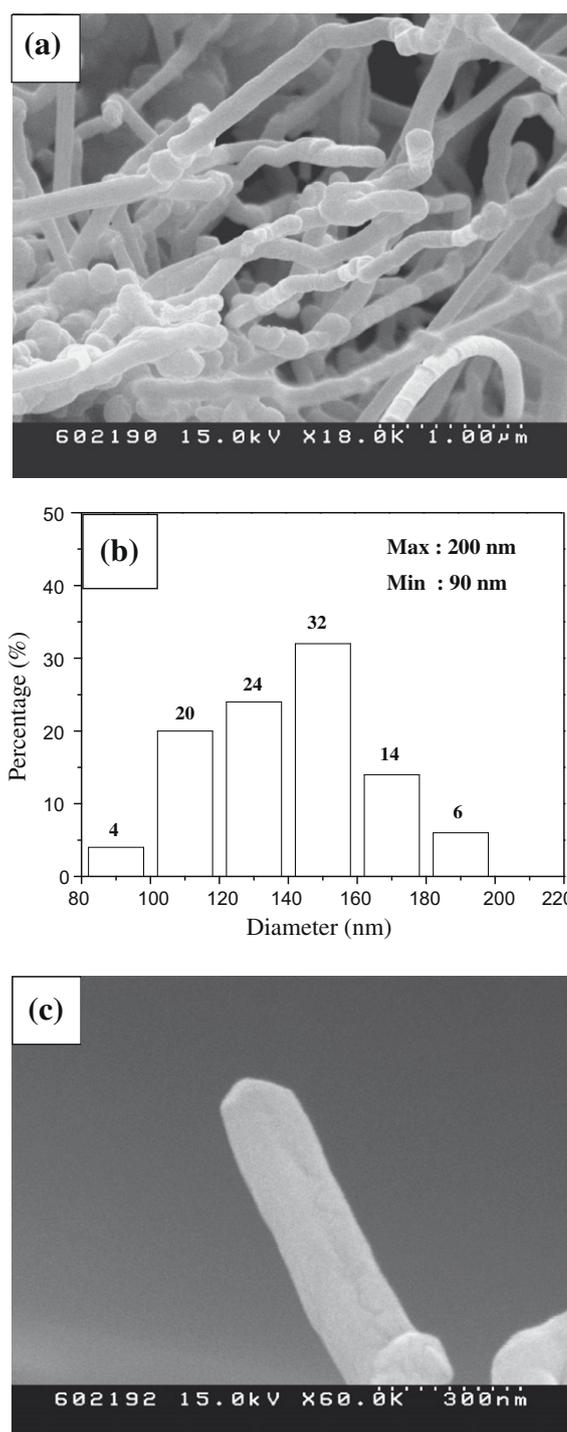
Fig. 1. (a) SEM image of the product. (b) Diameter distribution of the 1D structures. (c) Enlarged SEM image showing the tip part of a nanowire.

come from the air leakage or the residual oxygen in N$_2$ gas. Although we have used a N$_2$ atmosphere during the evaporation process in the furnace, there should exists the air leakage or the residual oxygen in the N$_2$ flow, consistent with the assertion made by Lee et al. [15] and the report of Kim et al. on the preparation of Ga$_2$O$_3$ nanowires from GaN powders in a N$_2$ atmosphere [16]. The other possibility is that additional oxygen comes from adsorbed oxygen in the tube, alumina boat, and substrates. Growth of crystalline structures via a VS mechanism is closely related to supersaturation degree of atoms in the gaseous state [17]. The growth of 1D
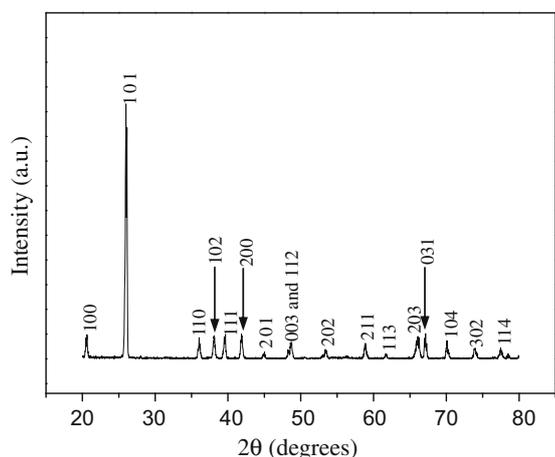
Fig. 2. X-ray diffraction pattern of the product.

structures is favorable under low supersaturation, whereas the nucleation occurs evenly to produce 2D or 3D structures under higher supersaturation. During the VS growth, the vapor species directly deposits on a substrate and grows into 1D nanostructures [18]. Initially, GeO_2 appears in the form of nanoparticles on the substrate, however, as the reactions continue, more atoms adhere to the surface of the nanoparticles [19]. There exists a competition in growth rate among different crystallographic planes at the initial stage of crystallization. However, once the condition which is favorable for the anisotropic 1D growth occurs, the atoms or species start to adsorb on a specific favorable advancing plane to invoke and continue the 1D growth [20]. It is known that the critical supersaturation degree depends on the growth conditions (such as growth temperature and pressure). We surmise that the supersaturation degree is sufficiently low under the process conditions in our present work, generating GeO_2 nanowires.

Fig. 4 shows the PL emission spectrum of the as-synthesized GeO_2 nanowires measured upon photoexcitation at 3.82 eV. In order to have more closer insights for the origin of emission, we have fitted the spectral feature with Gaussian functions. The best fit of the emission was obtained with two Gaussian functions, with the peaks being centered at 2.45 eV (507 nm in blue–green region) and 2.91 eV (427 nm in blue region), respectively. Similar blue–green emission and blue emission were observed in the PL spectra, respectively, from GeO_2 fibers prepared by electrospinning method [21] and from GeO_2 nanowires fabricated by the carbothermal reduction reaction [9]. They suggested that blue and blue–green light emissions are originated from radiative recombination in regard to defects in GeO_2, including oxygen vacancies and oxygen–germanium vacancy centers. In the present work, GeO_2 nanowires were synthesized at high temperature (900 °C) and GeO is 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 above-mentioned radiative recombination.

Fig. 5 shows the Raman spectrum of GeO_2 nanowires synthesized on Si substrate. The peak at 521 cm^{-1} is attributed to the optical phonon mode of the Si substrate [22]. Also, the peak at 443 cm^{-1} is related to the crystalline GeO_2 [23]. In addition, we observe a peak at 301 cm^{-1}. With the assumption that this peak is different from the optical phonon mode of Si at 299 cm^{-1}, we surmise that 301 cm^{-1}-peak corresponds to Ge optical phonons, being related to Ge–Ge bonds [23]. Since XRD pattern shown in Fig. 2 exhibits a hexagonal GeO_2 phase only, it is possible that there exists a trace amount of non-crystalline Ge in the product. Further study is necessary.
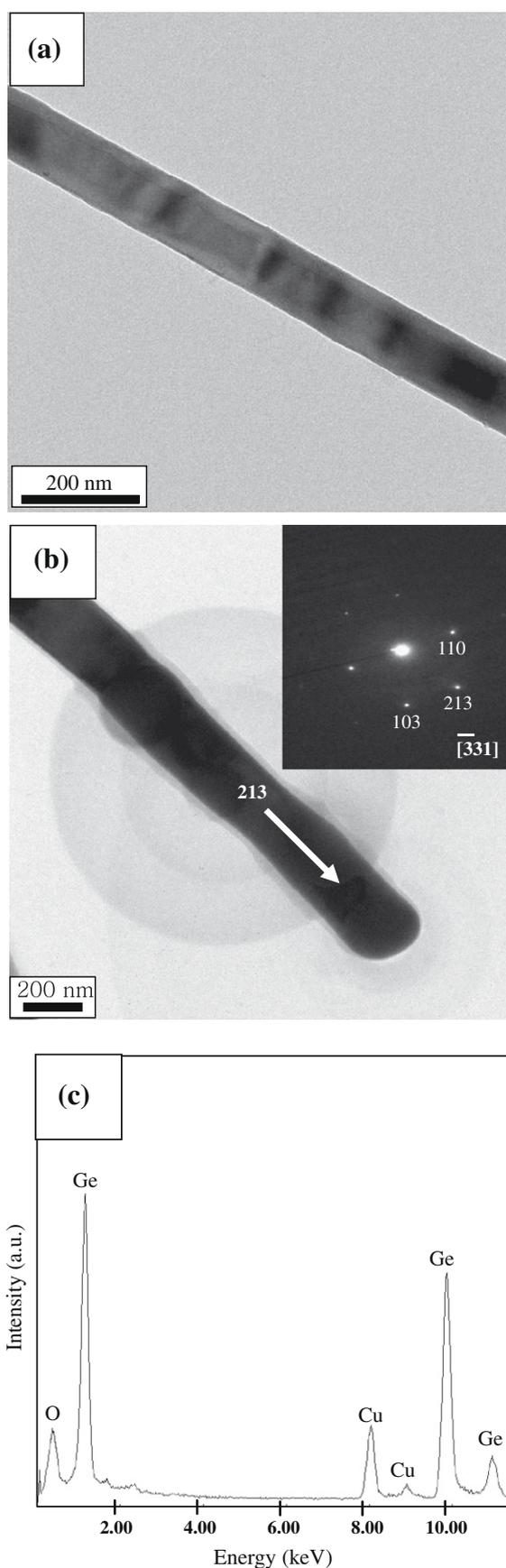

Fig. 3. TEM images showing (a) stem part and (b) tip part of GeO_2 nanowire, respectively. The inset corresponds to an associated SAED pattern. (c) EDX spectrum revealing that the nanowires are composed of Ge and O elements.
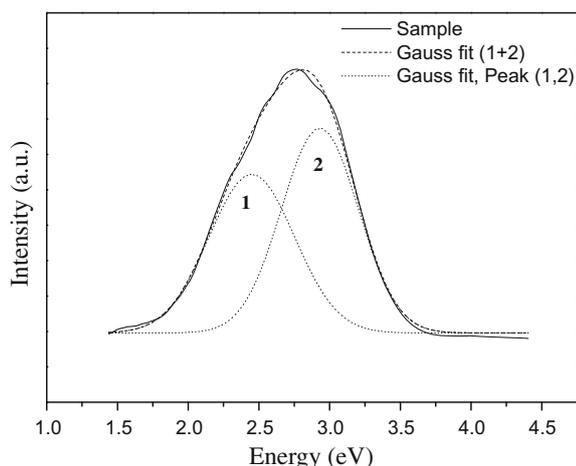
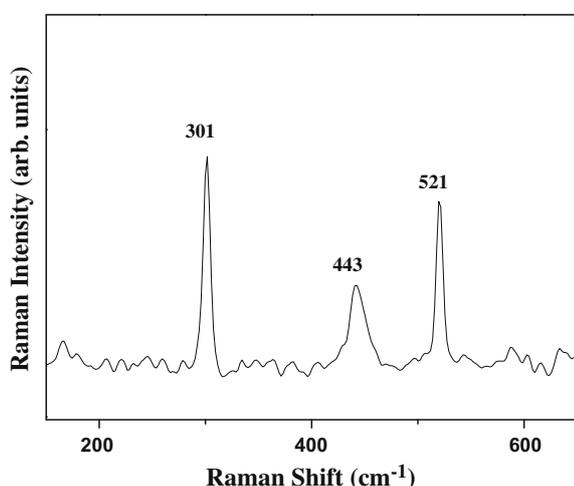**Fig. 4.** Photoluminescence spectrum upon photoexcitation at 3.82 eV.

Fig. 5. Raman spectrum of GeO₂ nanowires on Si substrates.

4. Conclusion

In summary, we have obtained GeO_2 nanowires by heating Ge powders at 900 °C in flowing nitrogen atmosphere. Characterizations using SEM, XRD, and TEM have been carried out to study the crystal structure and morphology of product, thereby demonstrating the fabrication of GeO_2 nanowires. The as-synthesized nanowires have diameter distribution from 90 to 200 nm. EDX spectroscopy reveals that the nanowires consist of Ge and O elements. XRD and SAED analyses coincidentally indicate that the obtained GeO_2 nanowires were crystalline with a hexagonal structure. The growth of GeO_2 nanowires is most likely controlled by the VS mechanism. The PL spectrum of the GeO_2 nanowires with a Gaussian fitting shows two emission bands at around 2.45 eV and 2.91 eV. Raman spectrum exhibits a GeO_2-associated peak, as well as peaks from Si substrates.

Acknowledgment

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