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Cone-shaped structures of GeO₂ fabricated by a thermal evaporation process

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Abstract

We have synthesized cone-like GeO₂ structures via thermal heating of Ge powders. We have investigated the effects of substrate temperature on the sample morphology, revealing that cone-shaped structures are preferentially obtained at higher temperature. The cone-shaped structures, which gradually become thinner to form a sharp tip, appear to be a single-crystalline, hexagonal structure of GeO₂. Room-temperature photoluminescence measurement revealed two emission peaks, at about 2.78 and 3.04 eV.

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1. Introduction

Germanium dioxide (GeO₂) is a dielectric oxide that is considered a promising material for a variety of applications. GeO₂ is an important material that exhibits a visible luminescence [1] while GeO₂-based glass is known to have a higher refractive index and higher linear coefficient of thermal expansion than those of SiO₂ [2], suggesting potential applications in future optical wave guides [3] and nanoconnections in optical devices and systems. Another important application of GeO₂ is in the area of vacuum technology [4].

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 [5], even if comprised of the same elements, it is worthwhile to fabricate new GeO₂ structures with different morphologies.

In particular, it has been observed that that cone-like structures with sharp tips significantly improve field emission qualities [6,7]. Accordingly, preparation of a cone-shaped structure is important not only for scientific interests but also

future industrial applications. However, to the best of our knowledge, no studies on cone-shaped GeO₂ structures have been reported. In the present work, we report on the synthesis of GeO₂ cone-shaped structures by a simple evaporation route, as well as their structural characterization and photoluminescence (PL) spectrum.

2. Experimental

A schematic diagram of the experimental apparatus can be found in [8]. 99.9%-pure Ge powders were used as the source material, being placed at the lower holder in the center of a quartz tube. As a starting material, we used standard polished p-type (1 0 0) Si wafers. The Si wafer was cut into small pieces with dimensions of 20 mm × 20 mm, and was subsequently blow-dried in N₂ gas. In order to fabricate Au-coated Si substrates, a layer of Au (thickness = 120 nm) was deposited by sputtering. The Si plate was placed at the upper holder with the Au-coated side downwards, serving as a substrate for collection of the growth products. The vertical distance between the powders and the substrate was approximately 10 mm. The furnace was heated to growth temperature in a range of 850–950 °C, and maintained at this temperature for 2 h under a flow of a nitrogen (N₂) and oxygen (O₂) gas mixture. The gas flow rates of N₂ and O₂ were 2000 and 20 sccm, respectively.

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The morphologies and crystal structure of the products were characterized using grazing angle X-ray diffraction (XRD: Cu $K\alpha_1$ radiation) (Philips X'pert MRD) with an incidence angle of 0.5° and scanning electron microscopy (SEM, Hitachi S-4200). Further structural analysis of individual structures was performed using transmission electron microscopy (TEM, Philips CM-200) with energy-dispersive X-ray spectroscopy (EDX) installed. For TEM observation, the product was ultrasonically dispersed in acetone, and a drop of the suspension was then placed on amorphous carbon films supported by copper (Cu) grids and dried in air. PL spectra of the samples were measured in a SPEC-1403 photoluminescence spectrometer with a He-Cd laser (325 nm, 55 mW) at room temperature.

3. Results and discussion

Fig. 1a shows a typical top-view SEM image of the product grown at 900°C . The products grown at 850 – 900°C mainly consisted of particles in an agglomerated state, with most particles being nearly spherical-shaped. A statistical analysis of many SEM images indicates that the diameter of particles produced at a growth temperature of 900°C was in a range of 500 – 1200 nm. Notably, the product grown at 950°C consists of cone-shaped structures with sharp tips (Fig. 1b). No catalyst particle can be seen at the tip of the cone-shaped structure grown at 950°C , as indicated in the upper right inset in Fig. 1b. Fig. 1c shows a side-view SEM image, revealing that the diameter of the structure decreases as the length of the structure is increased from bottom to top, with no particle at the tip. The cone-shaped structures have an almost straight-line morphology. It should be noted that there exist some cluster-like structures under the cone-shaped structures (indicated by black arrow).

The XRD pattern shown in Fig. 2 reveals the overall crystal structure of the product synthesized at 950°C . Apart from the Au-related peaks, which originate from the underlying substrate, all recognizable diffraction peaks including $(1\ 0\ 0)$, $(1\ 0\ 1)$, $(1\ 1\ 0)$, $(1\ 0\ 2)$, $(1\ 1\ 1)$, $(2\ 0\ 0)$, $(2\ 0\ 1)$, $(1\ 1\ 2)$, $(2\ 0\ 2)$, $(2\ 1\ 0)$, $(2\ 1\ 1)$, $(1\ 1\ 3)$, $(2\ 0\ 3)$ or $(2\ 1\ 2)$, $(3\ 0\ 1)$, $(0\ 1\ 4)$, and $(3\ 0\ 2)$ can be clearly indexed to the hexagonal structure of GeO_2 with lattice constants of $a = 4.987\ \text{\AA}$ and $c = 5.652\ \text{\AA}$ (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 the underlayer or substrate. Since the XRD spectrum was not dependent on the growth temperature in the range of 850 – 950°C , it is determined that the products are pure GeO_2 phase, regardless of the structural morphology.

TEM was employed to further analyze individual cone-shaped structures. EDX spectra indicated that the structures consist of Ge and O elements, regardless of the location in the structure from the stem to the ends (not shown here). Fig. 3a exhibits a typical high resolution TEM (HRTEM) lattice-resolved image, further revealing that the cone-shaped structures are structurally uniform and single crystalline, with interplanar spacings of 0.25 and 0.17 nm corresponding to $\{1\ 1\ 0\}$ and $\{1\ 0\ 3\}$ planes of hexagonal crystalline GeO_2 , respectively. Selected area electron

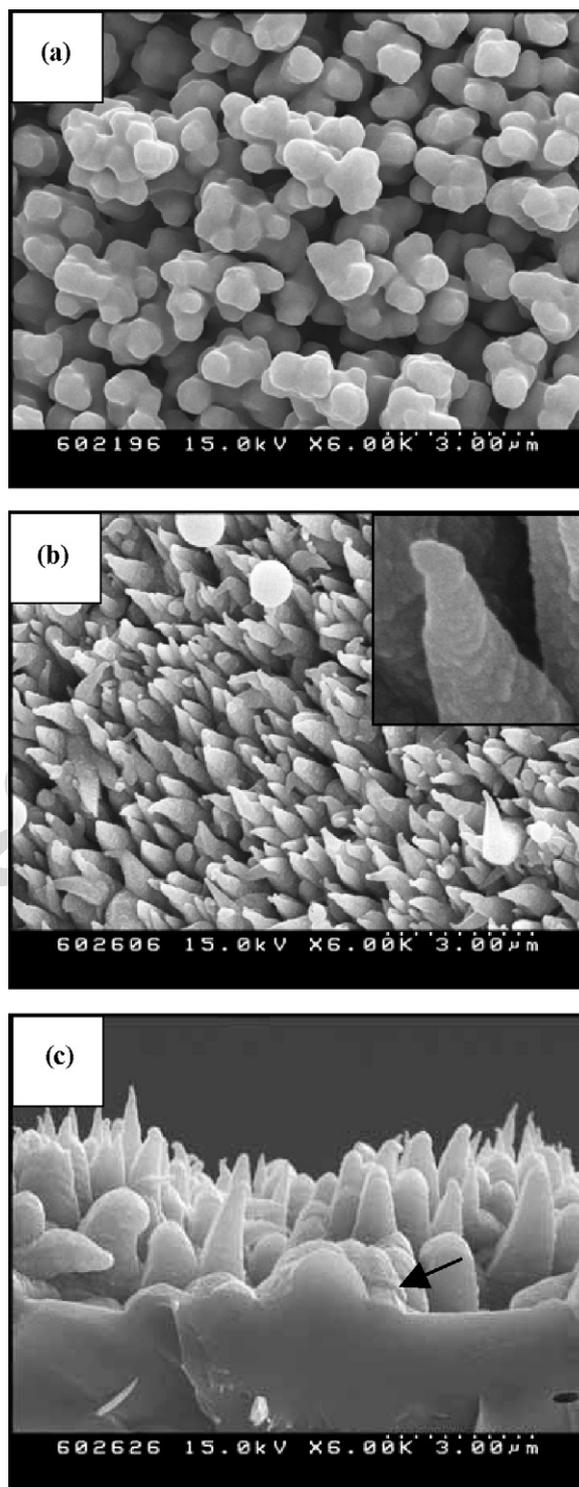


Fig. 1. Top-view SEM images of the products synthesized at (a) 900°C and (b) 950°C (inset: enlarged image showing an end part of a cone-shaped structure). (c) Side-view SEM image of the product synthesized at 950°C .

diffraction (SAED) measurement (Fig. 3b) demonstrates the single-crystalline nature of the structure. The diffraction spots can be indexed as $(1\ 1\ 0)$, $(1\ 0\ 3)$, and $(2\ 1\ 3)$ reflections for the $[\bar{3}\ 3\ 1]$ zone axis according to the hexagonal structure of GeO_2 .

Among two widely accepted mechanisms for the growth of 1D structures, vapor–liquid–solid (VLS) growth is a catalyst-

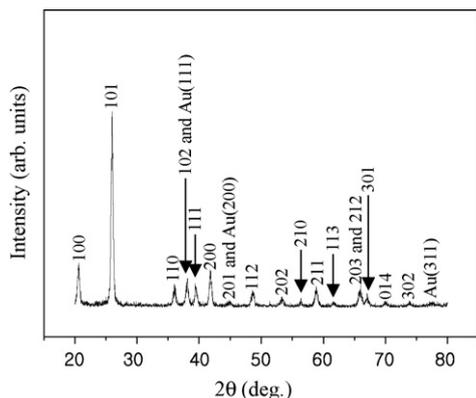


Fig. 2. XRD pattern recorded from the product synthesized at 950 °C.

assisted process, in which a metal catalyst particle acts as a liquid-forming agent. In the present work, SEM images, TEM images, and EDX analysis all indicate that the tips of the cone-shaped structures are free of metal particles. Hence, the vapor–solid (VS) mechanism may be more valid than the VLS mechanism in terms of explaining the growth of the GeO₂ cone-shaped structures. Regarding the vapor-phase reaction system for GeO₂ growth, it is generally agreed that GeO₂ forms at the initial stage of oxidation of Ge vapor ($\text{Ge(g)} + \text{O}_2\text{(g)} \rightarrow \text{GeO}_2\text{(s)}$). The Ge source can be continuously evaporated to form Ge vapor at a sufficiently high growth temperature, whereas the most likely source of oxygen is O₂ in the carrier gas, which can supply a constant oxygen source during the growth process. Subsequently, GeO₂ further reacts with Ge vapor to form GeO ($\text{GeO}_2\text{(s)} + \text{Ge(g)} \rightarrow 2\text{GeO(g)}$). Since the growth temperature is higher than the sublimation temperature of GeO (710 °C), we speculate that the formed GeO is in a gaseous phase. The GeO vapors are subsequently deposited on the substrates. The nuclei further grow, being oxidized to form GeO₂ cone-shaped structures in the oxygen environment in the tube.

Since the cone-shaped structures were grown on top of cluster-like structures (Fig. 1c), we deduce that the GeO₂ clusters were formed at an early stage of the synthesis process. When the synthesis was carried out under the same conditions at a lower substrate temperature, the as-synthesized product showed a cluster- or particle-like morphology without any cone-shaped structure (Fig. 1a). Thus, it is possible that the cluster-like structures observed in the present study (Fig. 1c) were formed while the temperature was elevated during the heating process. Subsequently, the anisotropic growth behavior, producing cone-shaped structures of a high aspect ratio, may be enhanced at higher substrate temperature (950 °C), possibly due to the faster diffusion of Ge and O species. Considering that the cone-shaped structures in the present study apparently grow via a VS process, we assume that the gradually diminishing Ge vapor supply could account for the tapering of the structure to form a sharp tip. It is possible that a higher-temperature process may result in earlier exhaustion of the Ge powder and/or may facilitate surface oxidation of the Ge powder, ultimately reducing the supply of Ge vapor. Similarly, several researchers attributed the formation of ZnO and SnO₂ needle-like

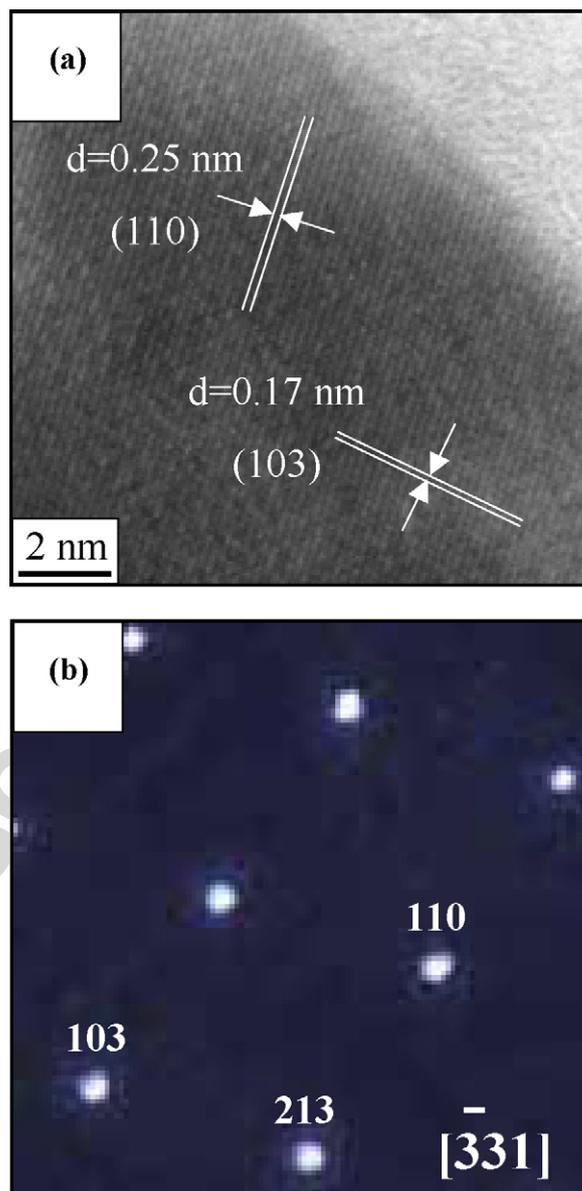


Fig. 3. (a) Typical HRTEM image of a cone-shaped structure, showing lattice fringes and (b) associated SAED pattern.

nanostructures to an exhaustion of Zn and Sn vapor sources, respectively [9–11]. Further investigation is necessary to elucidate the mechanism in detail.

Fig. 4 shows a room temperature PL spectrum of the as-prepared cone-shaped structures upon photoexcitation at 3.82 eV. In order to obtain greater insight into 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, of which peaks are centered at 2.78 and 3.04 eV, respectively. The PL peaks with energy of 2.78 and 3.04 eV correspond to approximately 447 nm in the blue region and 409 nm in the violet region, respectively. Violet emission has been previously observed in the PL spectra from GeO₂ powders [2], tetragonal GeO₂ layers [12], and GeO₂-containing films [13], whereas blue emission has been reported from 1D nanostructures of GeO₂ [2,14–16]. The blue light emission is

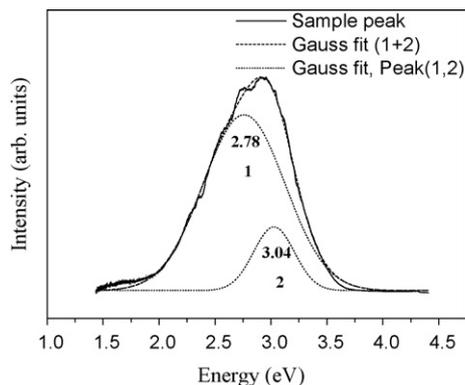


Fig. 4. Photoluminescence spectrum of as-prepared cone-shaped structures measured at room temperature upon photoexcitation at 3.82 eV.

attributed to radiative recombination between electrons in oxygen vacancies (V_{O^x}) and holes on germanium–oxygen vacancies centers (V_{Ge} , V_{O^x}) [2,15]. The violet light emission could possibly be ascribed to oxygen deficient luminescence centers [12]. Since the GeO_2 structures are prepared at high temperature, it is reasonable to assume that various defect centers such as oxygen vacancies exist in the product. Because of these PL emission properties, the GeO_2 structures may have potential application in future integrated optical devices.

4. Conclusions

In summary, we have prepared GeO_2 structures by heating Ge powders under air flow. Characterization using SEM has been carried out to study the morphology of the product, demonstrating that novel, cone-shaped GeO_2 structures were obtained by controlling the substrate temperature. EDX spectroscopy reveals that the cone-shaped structures consist of Ge and O elements. XRD, SAED, and HRTEM analyses

coincidentally indicate that the obtained GeO_2 cone-shaped structures are crystalline with a hexagonal structure. The growth of the GeO_2 cone-shaped structure is most likely controlled by a VS mechanism. The PL spectrum with a Gaussian fitting shows two emission bands, at approximately 2.78, and 3.04 eV, thus pointing toward potential applications in future optoelectronic devices.

Acknowledgement

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