



## Polycrystalline tubular nanostructures of germanium

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Received 9 April 2005; received in revised form 24 August 2005; accepted 25 August 2005

Communicated by D.W. Shaw

### Abstract

The saturated vapor adsorption (SVA) method is adopted to fabricate nanorods, nanotubes, and special nanostructures with the assistance of template. Here, germanium tubular structures with several diameters (50–200 nm) were produced with porous anodic alumina (PAA) template via SVA. The germanium tubular structures grew inside the nanopores, whose size agreed with that of Ge nanotubes, and then expanded to outside of PAA template, forming pipette-like structures. The Ge tubular structure growth process can be explained by both the vapor–solid and oxide-assisted growth mechanisms, which is different from the mechanism for nanorod growth.

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PACS: 73.63.Fg; 78.55.Mb; 81.10.Bk

Keywords: A1. Nanostructures; A2. Growth from vapor; B2. Semiconducting germanium

The discovery of carbon nanotubes in 1991 initiated extensive researches on quasi-one-dimensional nanostructures [1]. Nowadays, nanotubes made from inorganic materials are getting increasing attention because of their interesting properties and potential applications [2,3]. In particular, several methods have been used to fabricate Si nanotubes, for example, chemical vapor deposi-

tion (CVD) [4], molecular beam epitaxy (MBE) [5], and thermal evaporation [3]. Germanium and silicon show several similarities in their structural and electronic properties. Although Ge nanowires and cable-like nanostructures have been fabricated by different methods [6,7], Ge tubular structures have not been observed as far as we know.

Template-based methods have been proved to be successful in the fabrication of nanotubes. There are typically two growth routes: (1) through the nanochannels in the porous materials such as porous anodic alumina (PAA) [4,5], liquid crystals

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(LCs) [8] and molecular sieves [9]; and (2) “epitaxial casting” using nanowires (such as ZnS [3] and ZnO [10]) as templates. We consider a phenomenological idea to grow nanostructures as shown in Fig. 1(a). In a sealed vacuum with high temperature (900–1200 °C), the vapor of source (Ge in our experiment) is full of space, including nanopores of template (Step I). After cooling (see Step II), it is expected that Ge vapor in nanochannels of template (PAA in our experiment) will form one-dimensional nanostructures because of the steric confinement. After careful investigation, the following nanostructures can be formed: (1) nanorods [11], (2) nanotubes, and (3) pipette-like tubular structures.

Here, we report the synthesis of Ge tubular structures on PAA template utilizing saturated vapor adsorption, during which the Ge gas pressure is saturated at high temperature in an airtight quartz tube. Germanium polycrystalline tubular structure of different diameters

(50–200 nm) are observed to grow both in the channels and out of the nanopores in PAA, and the results are confirmed by pipette-like tubes.

A PAA template with ordered nanopores of about 55 nm was produced by a conventional method [12]. The source materials for fabrication are a small tablet of Ge and powders of GeO<sub>2</sub>. They are sealed together with the PAA template in a quartz tube with a 10<sup>-3</sup> Pa vacuum. The Ge tablet and GeO<sub>2</sub> are mixed and have a distance of 10 cm away from the PAA template. The sealed quartz tube was then heated uniformly to 1100 °C for about 3 h and then remained in vacuum for 10 h during which time the sample cooled. During the heating process, the tube was filled with the autogenous vapor pressure of germanium.

The sample was subsequently milled for several minutes using the Ar<sup>+</sup> milling method and checked by scanning electron microscopy (SEM), because the tip of tube is closed like a carbon nanotube. As shown in Fig. 1(b), it reveals that Ge

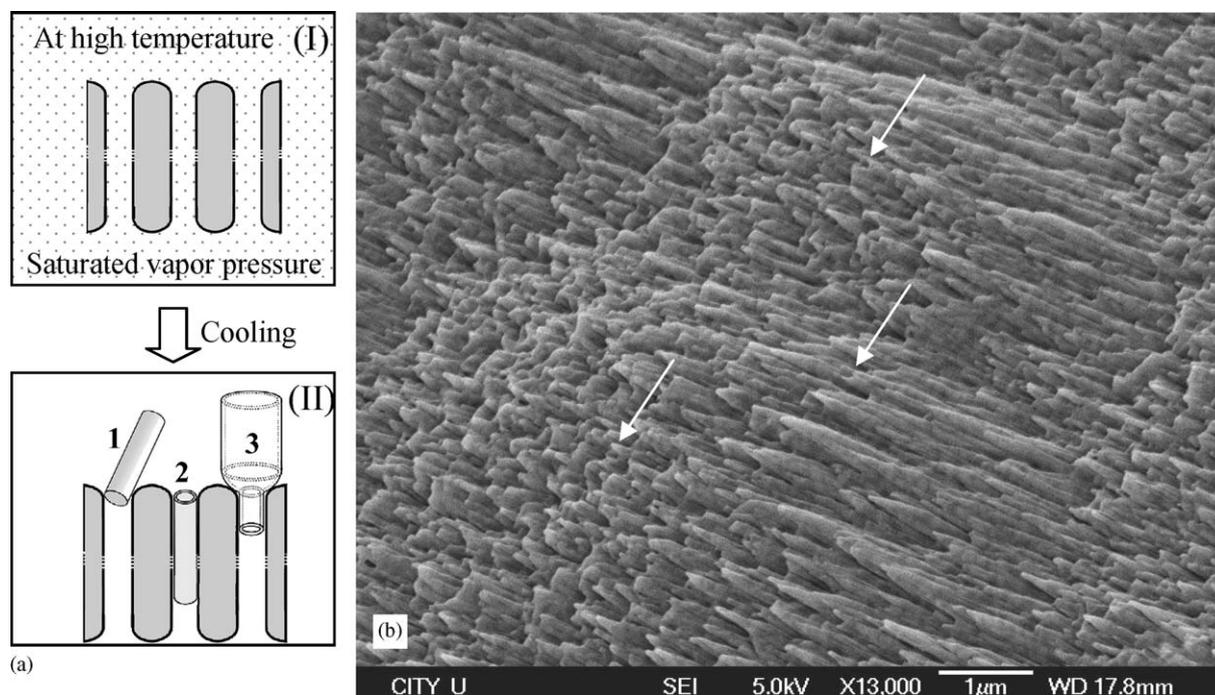


Fig. 1. (a) Schematic diagram of the process describing the formation process of Ge (1) nanorods, (2) tubular structures, and (3) pipette-like tubes; (b) SEM image of Ge tubular structures grown on porous anodic alumina template after the sample was milled using ion milling method for several minutes.

tubular structures are grown on PAA template and some tubular structures is shown by the white arrows.

The samples without any ion milling were grinded into powders and immersed in a 5 M NaOH solution for several hours. The solution was then put onto a carbon-coated specimen grid for transmission electron microscopy (TEM, Philips CM20) measurement after condensation. If the powder was directly held with a carbon-coated specimen grid and subsequently observed by TEM, there also exist the tubular structures. So the effect of NaOH solution can be neglected in our experiment. Figs. 2(a)–(d) reveal that Ge tubular structures have been formed on the PAA template. Fig. 2(a) depicts a TEM image of the Ge tubular structure with a split at one end of the tube and a schematic diagram. Its other end is embedded into the alumina matrix, as confirmed by our other observations to be discussed below. Figs. 2(b)–(d) show a series of TEM micrographs obtained at different tilting angles corroborating the successful synthesis of the Ge tubular structures. The selected-area electron-diffraction (SAED) pattern of the area marked with a circle in Fig. 2(e) shows the crystalline structure of germanium as indexed [6,7]. Fig. 2(f) shows the high-resolution TEM (HRTEM, JEOL 2010) image of an individual Ge tubular structure. Figs. 2(g) and (h) demonstrate that the wall and center of the tubular structure are in polycrystalline structure and with the (1 1 1) lattice spacing of 3.26 Å and (2 2 0) of 1.97 Å, which well agree with that of germanium. At the edge of the tube little oxide exists as shown in Fig. 2(g), while there is little amorphous structure among Ge crystal which may be Ge oxide. Comparing to the growth of Ge monocrystalline nanorod [11], we think that vapor-solid (VS) mechanism dominates the growth of tubular structures with the oxide assistance.

Ge tubular structures of different diameters of 50, 120, and 200 nm can be observed in Figs. 3(a), (b) and (c), respectively. The SAED patterns are displayed in the insets of each TEM images. The crystallinity of large Ge tubular structures is better than that of small ones comparing the SAED patterns. More crystalline structure with the [1 1 1] orientation can be observed in the Ge tubular

structure with a diameter of 200 nm because the intensity of the [1 1 1] ring is much stronger than the others. In addition, a special structure resembling a pipette-like tube is revealed by TEM [Figs. 4(a)–(c)]. The diameter of the Ge tubular structure at the bottom end is about 50 nm [Fig. 4(b) shows a small tip with size of about 50 nm]. The other end with a large diameter is about 150, 190, and 210 nm, respectively, as shown in Figs. 4(a), (b), and (c).

To explain the formation of the tubular structures and pipette-like tube, we propose a simple model as shown schematically in Step II of Fig. 1(a). The tubular structures grow along the channel in the PAA initially, and so the small end shows a diameter of about 50 nm as shown in Figs. 4(a) and (c), and it corresponds to the diameter of the nanopores in the PAA template. In Fig. 4(b), although no small tube can be observed, a tip smaller than 50 nm is revealed. In order to investigate the growth mechanism of our pipette-like tubes, we checked the large (I) and small (II) ends in Fig. 4(c) by SAED measurements as shown in Fig. 4(d). The large and small ends displayed polycrystalline structure with (1 1 1) orientation and (2 2 0) orientation, respectively. Larger Ge nanostructures (large end) prefer growth (1 1 1) direction, while smaller Ge nanostructures (small end) are almost exclusively (2 2 0). So we believe that these behaviors may reflect their different surface and interface energies, which is consistent with the growth of Si nanowires with various diameters [13].

Based on the Wilson–Frenkel growth law [14], there is a critical size (about 10 nm) for the growth of one-dimensional nanostructures inside carbon nanotubes calculated by a nanothermodynamic model [15]. In our results, the wall of the large end of a pipette-like tube has the thickness of larger than 10 nm, while that of the small end is about 10 nm by our careful verification. During our experiments, the general growth conditions for both ends are the same, such as temperature  $T$  and pressure  $P$ . However, other parameters, such as surface and interface tension are different because of the nanochannels in PAA template. So we believe that the interface tension between Ge nanostructures and the walls of nanochannels play

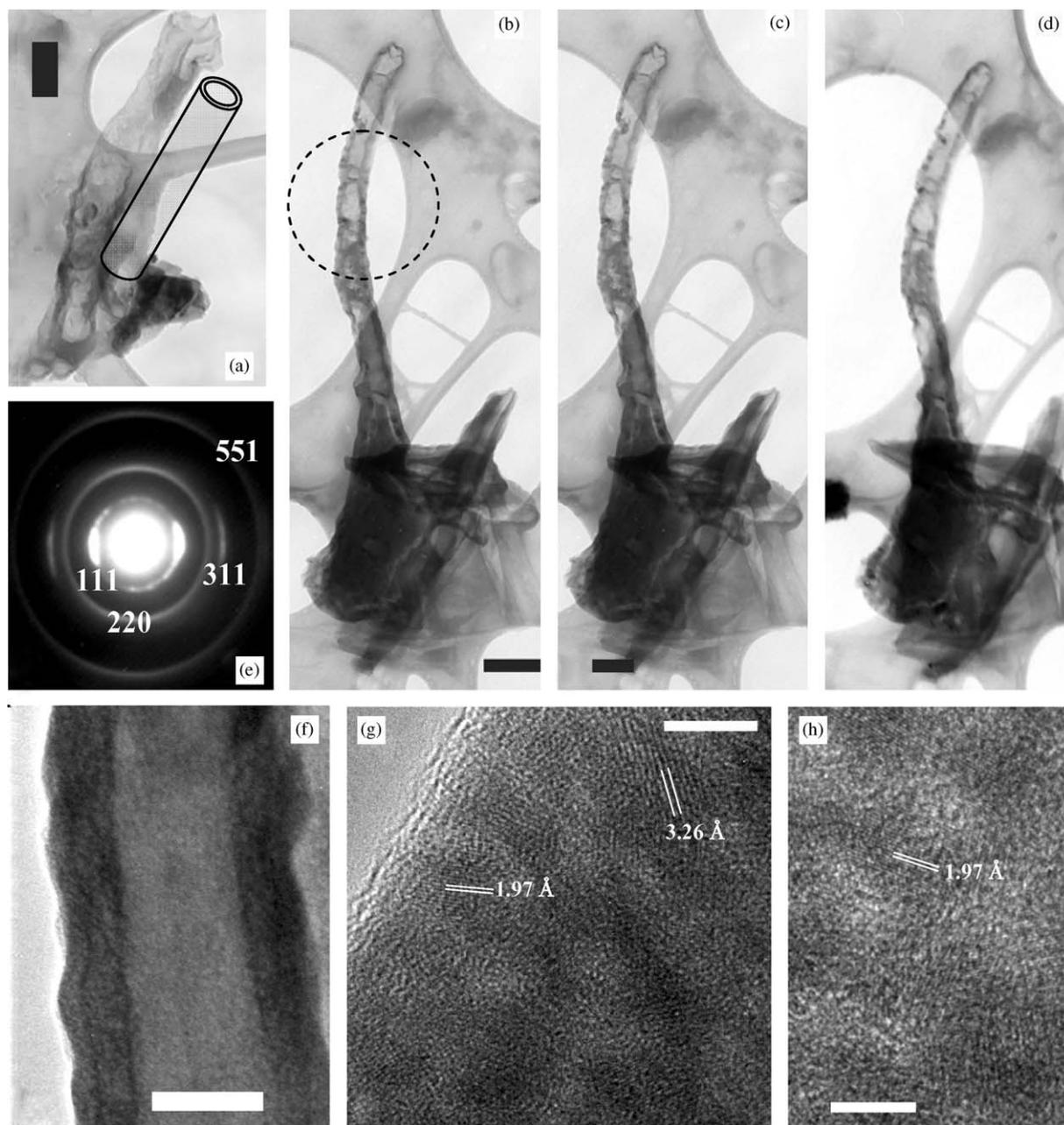


Fig. 2. TEM images of: (a) Ge tubular structure exhibiting a split on one end of the tube and the related schematic diagram; a series of TEM micrographs acquired at different tilt angles from an individual Ge tubular structure: (b)  $+20^\circ$ , (c)  $0^\circ$ , and (d)  $-30^\circ$ ; (e) the selected-area electron-diffraction (SAED) pattern of a circle area as shown in (b); the high-resolution TEM images of an individual Ge tubular structure (f), tube wall (g), and the center (h) of Ge tubular structure. The scale bar corresponds to: (a) 200 nm; (b)–(d) 500 nm; (f) 50 nm; and (g), (h) 5 nm.

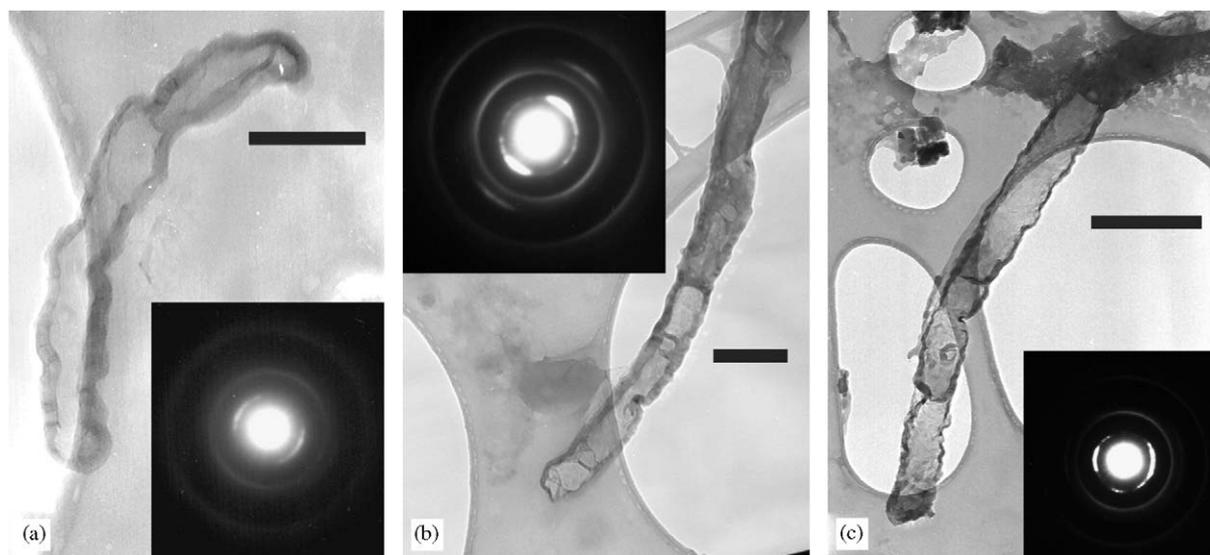


Fig. 3. Ge tubular structures with different diameters: (a) 50 nm, (b) 120 nm, (c) 200 nm, and their corresponding SAED patterns (the insets) [The scale bar is (a) 100 nm, (b) 200 nm, and (c) 500 nm].

an important role in the formation of Ge pipette-like tubes.

With regard to the growth process, the vapor–liquid–solid (VLS) mechanism should be excluded for no spherical nanoparticles could be found at the tips of the tubes in our results [7,16]. Hence, the VS [17] and oxide-assisted growth (OAG) [18] mechanisms are more likely. The solid Ge tablet is evaporated during the heating process and the quartz tube as well as the channel in PAA template are filled with saturated germanium vapor because it is airtight and under vacuum. The germanium gas inside the channel in the PAA template is nucleated when the temperature drops. With an adequate supply of precursor gas, Ge nanorods are observed to form [11]. Deficiency of Ge vapor in the nanopores induces the formation of Ge tubular structures and it appears that the VS mechanism is responsible for the growth. However, no tubular structures can be formed without  $\text{GeO}_2$  as the source. Hence, we propose that the growth of the polycrystalline tubular structures is governed by both VS and OAG. Initially, Ge and  $\text{GeO}_2$  vapor forms when heated to  $1100^\circ\text{C}$ . Due to the residual oxygen in the tube from the decom-

posed  $\text{GeO}_2$  at high temperature [19], a portion of the Ge and  $\text{GeO}_2$  vapor is further oxidized to form  $\text{GeO}_x$  ( $\text{Ge} + x\text{GeO}$ ) [7]. In our experiments, the  $x$  value is small because the quantity of  $\text{GeO}_2$  is small and the vacuum is high. The  $\text{GeO}_x$  vapor then adsorbs onto the channel in the PAA template and formation of the tubular structures ensues.

In summary, Ge tubular structures and pipette-like tubes of different diameters were produced on the PAA template employing saturated vapor. The tubular structures can be formed both in the channels and out of the nanopores in the PAA as confirmed by pipette-like tubes. The formation of the tubular structures can be explained by both the VS and OAG mechanisms.

We thank Mr. M.K. Tang and Dr. Amy X.Y. Lu for experimental assistance. This work was supported by grants (Nos. 10225416 and BK2002077) from the Natural Science Foundations of China and JiangSu province as well as Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grants (CERG) # CityU1052/02E and # CityU1137/03E.

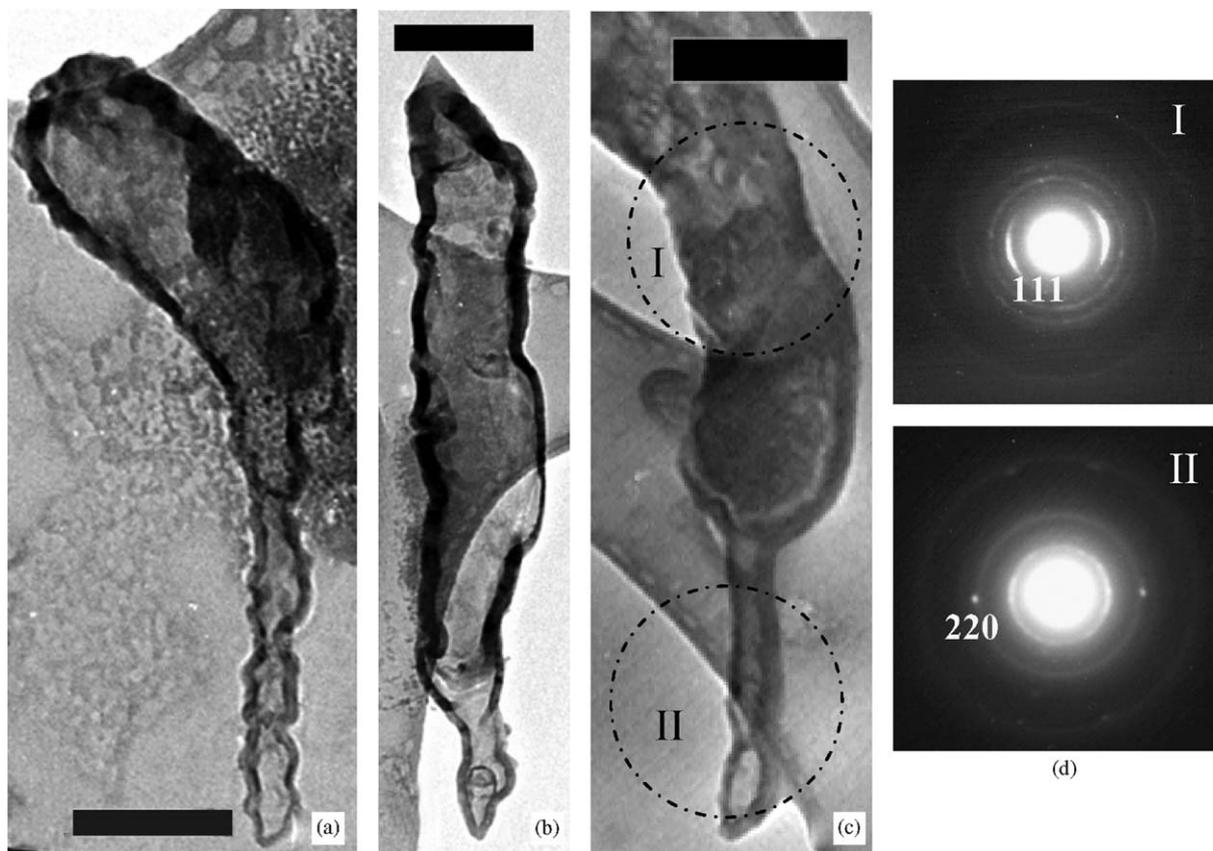


Fig. 4. (a)–(c) Pipette-like tubes of germanium; (d) SAED patterns of area I and area II in (c) [the scale bar is (a) 200 nm, (b) 250 nm, and (c) 250 nm].

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