Synthesis and Optical Properties of Gallium Phosphide Nanotubes

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Gallium phosphide nanotubes with zinc blende structure were synthesized for the first time. The as-prepared GaP nanotubes are polycrystalline with diameters of 30−120 nm and occasionally partially filled. The growth has been reasonably proposed to follow vapor−liquid−solid (VLS) mechanism. The integration of the nanotubular structure with the unique intrinsic semiconducting properties of GaP might bring GaP nanotubes some novel optical and electronic properties and applications.

1. Introduction

Nanotubes have attracted increasing attention due to their great prospects in the fundamental physical sciences and modern nanotechnology arising from the unique nanotubular structures and quantum confinement effects.[1] Since the discovery of carbon nanotubes,[2] many efforts have been devoted to exploring new nanotubular structures of other substances,[3] and the nanotubular family has been rapidly extended to numerous layered compounds including nitrides,[4] chalcogenides,[5] halogenides,[6] and so on for evenly bent nanotubes, and very recently to nonlayered compounds such as GaN,[7] AlN,[8] ZnO,[9] and Te[10] for faceted nanotubes. Some promising properties such as hydrogen storage,[11] field emission,[12] and superconductivity[13] have been discovered, and some prototypes of advanced nanodevices such as field effect transistors,[14] sensitive biochemical sensors,[15] and tips in scanning probe microscopy[16] have also been developed.

Among the nanotubular family, the semiconductor nanotubes of III−V compounds are particularly interesting because these series of compounds provide adjustable direct band gaps from 0.17 eV in InSb to 6.2 eV in AlN.[17] Hence, ultimate nanoscale optoelectronic devices for a wide range of wavelengths with many advanced features such as high thermal conductivity and superior stability may be realized by using these nanotubular structures. However, to our knowledge, the obtained nanotubes of this system are still restricted to a few members of GaN,[7] AlN,[8] InN,[18] and InP[19] to date. As a popular semiconductor with a wide band gap of 2.26 eV, gallium phosphide has been found to be an important candidate for light emission devices in the visible range.[20] GaP nanowires[21−23] and nitrogen-doped nanobelts[24] have been obtained by different preparation methods recently. In this letter, the synthesis and characterization of GaP nanotubes are reported. The as-prepared GaP nanotubes are polycrystalline with zinc blende structure, and the formation mechanism is reasonably proposed.

2. Experimental Methods

The GaP nanotubes are produced through a chemical reaction with Ga and Ga_2O_3 as the Ga source, red phosphorus as the P source, and AlN (e.g., AlN nanowires) as the reducer. The preparation of GaP nanotubes was conducted in a tubular furnace at elevated temperature. In a typical run, Ga, Ga_2O_3 powder, and red phosphorus are mixed with the mole ratio of 4:1:6 and grinded in mortar for 10 min. The mixture precursor (0.5 g) was placed at the upstream end of a small quartz tube with the inner diameter of 1 cm and length of 10 cm. About 0.1 g AlN nanowires of about 15 nm in diameter, which were prepared via the extended vapor−liquid−solid (VLS) growth[25] (see Figure S2 of the Supporting Information), were put on the downstream end of the small quartz tube as the reducer. The quartz tube with the two ends loosely plugged with glass fiber was mounted in the tubular furnace, heated to 1030 °C in argon, and held there for 3 h. Then the furnace was cooled to room temperature, and the product was collected for characterization.

X-ray diffraction (XRD) experiments were operated on a Philips X'pert Pro X-ray diffractometer with Cu Kα radiation of 1.5418 Å. The morphology, structure, and component of the product were analyzed by transmission electron microscopy (TEM, JEOL-JEM-1005 at 80 kV) and high-resolution transmission electron microscopy (HRTEM, JEM2010 at 200 kV) with an energy-dispersive X-ray analyzer (EDX, Thermo NORAN) attached. The grid specimen was prepared by ultrasonic treatment to the product in the aqueous solution of ethanol for dispersion. The optical properties of the product were investigated by Raman spectroscopy (JY-HR-800, excited with an Ar$^+$ line at 514 nm) and photoluminescence spectroscopy (SLM48000DSCF, excited with a He−Cd laser at 442 nm) at room temperature.

3. Results and Discussion

Figure 1 is the typical TEM images of the product. In addition to the unconsumed reducer of AlN nanowires with diameters of about 15 nm, some nanotubes are clearly observed with a diameter of about 30−120 nm and a thickness of about 10 nm.

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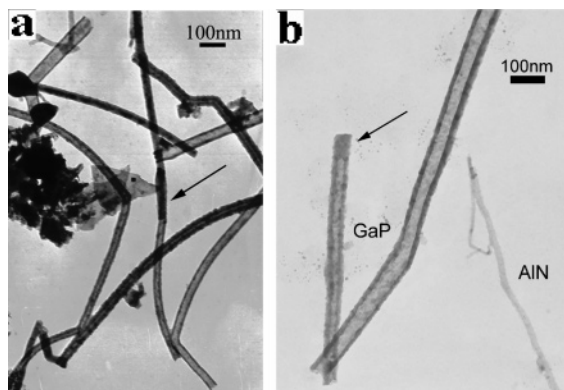
Figure 1. Typical TEM images of the as-prepared product. The filled location is marked with an arrow. (a) Several nanotubes with different diameters; (b) coexistence of nanotubes with unconsumed AlN nanowires. The diameters of the nanotubes (product) are clearly larger than those of AlN nanowires (reactant).
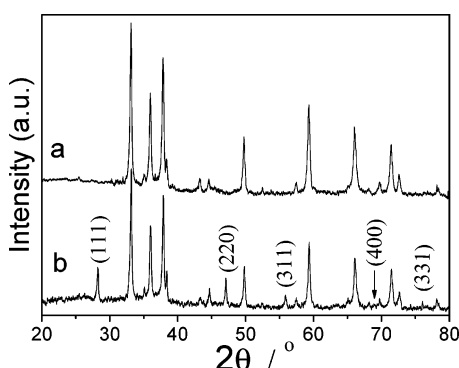

Figure 2. XRD patterns of (a) the reducer of AlN nanowires and (b) the as-prepared product. The indices corresponding to the diffraction peaks of GaP with zinc blende structure are marked, respectively. The unmarked peaks arise from hexagonal AlN.

These nanotubes are easily distinguished from the AlN nanowires with much smaller diameters. Some partially filled nanotubes are also noticed, which will be discussed later.

Figure 2 shows the XRD patterns of the reducer of AlN nanowires (a) and the as-prepared product (b). It is seen that an additional set of diffraction peaks which could be well-assigned to GaP with zinc blende structure (JCPDS: 32-397) appear in Figure 2b for the product in comparison with Figure 2a for AlN nanowires. In combination with the TEM results, it is learned that GaP nanotubes are produced.

To learn more about the novel tubular nanostructure of GaP, high-resolution TEM was employed to characterize the as-prepared nanotubes, as shown in Figure 3. The contrast between the tube wall and the inside hollow region could be clearly identified from Figure 3a. The wall thickness of the nanotube is about 10 nm, and the wall surface is rather rough. The high-resolution image (Figure 3b) shows that the nanotube wall is composed of many tiny crystallites with grain sizes of ca. 5 nm with different orientations, indicating the polycrystalline structure of the nanotube. This is confirmed by the starry electron diffraction (ED) pattern as shown in Figure 3c. The spacing between the neighboring fringes of a particle is 0.318 nm, corresponding to the d value of (111) planes of zinc blende GaP. All of these results verify that the polycrystalline zinc blende GaP nanotubes are obtained. An amorphous layer of the Al_2O_3 byproduct was also observed on the surface of the GaP nanotubes (see Figure S3 of the Supporting Information).

Raman spectrum of the as-prepared sample in Figure 4a shows the Raman-active modes of transverse optical (TO)
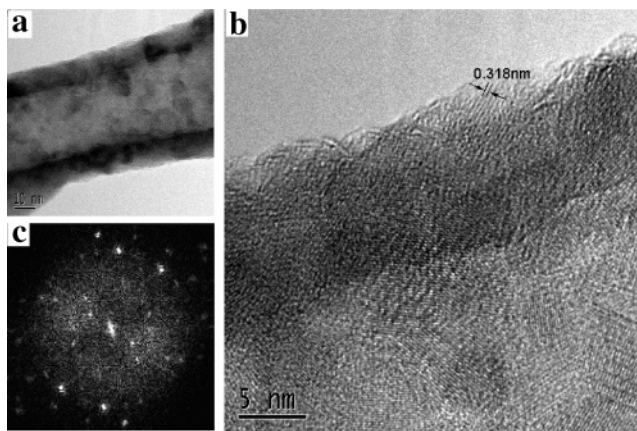

Figure 3. Typical TEM images of the as-prepared GaP nanotubes. (a) Overview of a section of a nanotube. (b) HRTEM image of the nanotube. (c) Corresponding ED pattern of the nanotube.
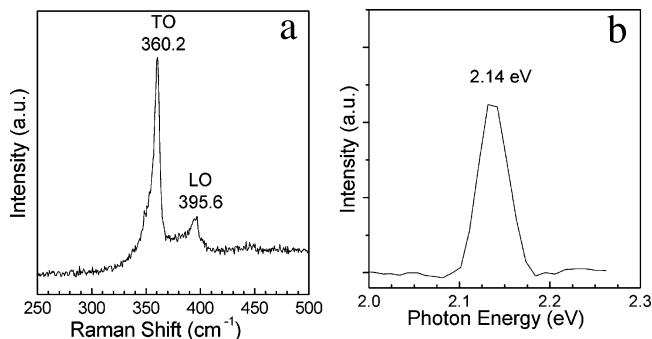

Figure 4. Raman (a) and photoluminescence (b) spectra of the product.

phonon and longitudinal optical (LO) phonon at 360.2 and 395.6 cm^{-1}, respectively, according with the corresponding values of 360 and 395 cm^{-1} for the zinc blende GaP nanorods with diameters around 22 nm.[22] Both peaks are broadened and asymmetrical in shape and show significant downshifts of ca. 5 and 7 cm^{-1} with respect to the TO and LO phonon modes of bulk or microcrystal GaP.[23] The broadened, asymmetrical, and downshift features of the Raman peaks may partially result from the quantum confinement effect and surface defects due to the Al_2O_3 coating.[22,23] In addition, it is noticed that the intensity ratio of the TO to LO peaks is unusually higher than that for the GaP microcrystals, nanowires, or nanobelts,[22−24] which may be correlated with, e.g., the more intensive internal stress or the lattice distortion due to the unique nanotubular structure. Figure 4b presents the photoluminescence spectrum of the product, which has a sharp peak centered at 2.14 eV. This green peak can be attributed to the direct band gap emission of GaP, a little bit red-shifted but in agreement with the emission of GaP nanowires.[23] The red shift of the emission peak may result from the surface Al_2O_3 impurity on the nanotubes, rather than from the size effects.[23] Detailed studies will follow to elucidate the energy downshift of the photoluminescence peaks. The optical characterization result indicates that these GaP nanotubes have potential applications in light emitting devices.

As mentioned before, partially filled nanotubular morphologies were also observed in the product as typically shown in Figure 5. Two typical picture contrasts are obvious, indicating two different filled substances. The "grey" substance as shown in Figure 5a has the same appearance in color as the nanotube wall, indicating another morphology of the GaP product as supported by the EDX characterization. The "dark" substance as shown in Figure 5b was confirmed to be metal gallium by the corresponding HRTEM image (see Figure S4 of the
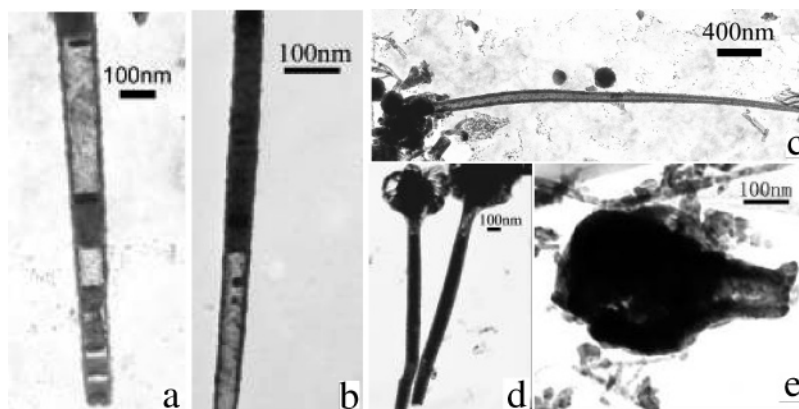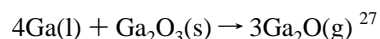
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Figure 5. (a−b) Typical TEM images of the partially filled GaP nanotubes, (c) a hollow nanotube grown from "ingredient supplier", (d) two partially filled nanotubes grown from ingredient suppliers, and (e) a detached ingredient supplier.

Supporting Information). Due to the low Ga content in the product, no signal of Ga could be detected in the XRD pattern in Figure 2.

Special attention has been paid to the end parts of the nanotubes as typically shown in Figure 5c−e, which could give us some clue about the growth mechanism. It is seen that the GaP nanotubes are grown from the "ingredient suppliers", which is similar to the case in VLS growth.[26] However, the dimensions of the ingredient suppliers are much larger than the diameters of the corresponding nanotubes. Figure 5c and d represent the two cases corresponding to the hollow and partially filled nanotubes, respectively. The ingredient supplier in Figure 5e might be detached from a nanotube during the cooling stage in synthesis or subsequent ultrasonic treatment for the TEM specimen.

According to the above experimental results, the growth mechanism or process for the formation of GaP nanotubes is proposed as follows. At a temperature of 1030 °C, the reaction between the precursors of Ga and Ga_2O_3 produced the gaseous species of Ga_2O,[27] which diffused to and were reduced by AlN. Ga species were then generated and aggregated into small liquid droplets in the interspaces of the AlN framework due to its low melting point of 29.8 °C and high boiling point of 2403 °C. Meanwhile, phosphorus vapor diffused into the Ga droplets and reacted to form GaP species within the droplets. This process could be represented as

$$4Ga(l) + Ga_2O_3(s) \rightarrow 3Ga_2O(g) \; ^{27}$$

$$3Ga_2O(g) + 2AlN(s) \rightarrow Al_2O_3(s) + 6Ga(l) + N_2(g)$$

$$P(g) + Ga(l) \rightarrow GaP(s) \text{ (nanotube)} \; ^{28}$$

When GaP species reached a supersaturated level, they were precipitated out from the Ga droplets, i.e., the ingredient suppliers, to form the GaP nanotubes in the manner similar to VLS growth.[26] Here, Ga droplets functioned as reactant as well as reaction medium.[29] P vapor and the newly produced Ga species were continuously complemented into the Ga droplets to sustain this growth, and finally the GaP nanotubes were obtained. When the complementing rate is larger than the consuming rate due to nanotube growth, the size of the Ga droplet would increase. Sometimes, some liquid Ga or GaP-containing Ga could be soaked inside the nanotubes through the connecting part during growing, probably due to the volumetric expansion of the Ga droplets or the capillarity effect,[30] leading to the partially filled nanotubes. The size changes of the Ga droplets (ingredient suppliers) during growth

due to the aforementioned factors such as complementing, consuming, or soaking could be the main reason for the diameter variations of the GaP nanotubes as observed, which favors the formation of polycrystalline rather than single-crystalline nanotubes.

This growth mechanism is supported by the results of the comparison experiments. As discussed above, the Ga droplets were generated via the reduction of Ga_2O by AlN; hence the reducer of AlN played an important role for the formation of GaP nanotubes. We substituted AlN nanoparticles for AlN nanowires under the same synthesis condition, and the GaP nanotubes could still be obtained. However, when AlN was substituted by γ-Al_2O_3 or Fe−Co/γ-Al_2O_3 powder, no GaP nanotubes were synthesized, and only the GaP particles could be observed in the product, which resulted from the gaseous reaction of Ga_2O with P (see Figure S5 of the Supporting Information).[28] In addition, after reaction, no GaP nanotubes but particles could be observed in the region for putting the mixture of Ga, Ga_2O_3, and P precursors although Ga and P existed there. This is because the granular Ga precursor is too big to reach the supersaturated level necessary for nanotubular precipitation.

The GaP nanostructures in the product should rely on the concentration of the GaP species in the ingredient supplier droplet, which mainly depends on the pressure of the P vapor. It is believed that the GaP nanostructure is controlled by the competition of the crystal growth rate at the liquid−solid interface with the diffusion of GaP species in the droplet.[19] High concentrations of the GaP species in the droplet would provide enough ingredient for the nucleation front at the liquid−solid interface through diffusion; hence, the growth takes place at the entire liquid−solid junction (kinetically limited), giving rise to GaP nanowires. On the contrary, a low concentration of GaP species in the droplet could not provide enough ingredient for the growth at the entire liquid−solid junction. The growth becomes diffusion-limited and the nucleation front is ring-shaped at the liquid−solid interface, giving rise to the growth of GaP nanotubes. Indeed, GaP nanowires have been synthesized in our comparison experiment, where excessive red phosphorus in the precursor was used; hence, the concentration of the GaP species in the droplet was increased. (see Figure S8 of the Supporting Information) This has an analogy with the cases for the growth of InP[19] and carbon one-dimensional nanostructures.[31]

4. Conclusions

In summary, polycrystalline GaP nanotubes with zinc blende structure were synthesized for the first time, and the growth

mechanism has been reasonably proposed. The integration of nanotubular structure with the unique intrinsic semiconducting properties of GaP might bring GaP nanotubes some novel optical and electronic properties and applications.

Supporting Information Available: Schematic experimental apparatus, the preparation process of AlN nanowire precursor, EDX results of GaP nanotubes, HRTEM image of partially filled GaP nanotube, the morphologies of GaP products prepared under different conditions, and the brief analysis of the Raman and photoluminescence spectra of the product. This material is available free of charge via the Internet at http://pubs.acs.org.

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