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Uniform and high-quality submicrometer tubes of GaS layered crystals

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GaS, group III–VI semiconductor compound, is known to possess a layered structure. In this letter, uniform and high-quality GaS submicrometer tubes have been synthesized via a simple high-temperature thermal reaction route. Each GaS tube is uniform in size, and has length up to tens of microns and outer diameter of \sim 200–900 nm; some of the tubes are partially filled with liquid metallic Ga "rods." Photoluminescence spectrum reveals that the GaS tubes have two strong emission bands centered at \sim 585 and \sim 615 nm. Possible reaction processes and a rolling-up growth mechanism of as-grown GaS tubes were briefly discussed. © 2005 American Institute of Physics. [DOI: 10.1063/1.2093924]

Following the discovery of a carbon nanotube,¹ an active research has been launched with respect to the formation of tubular structures in other layered or anisotropic crystals. Tenne *et al.*² succeeded in the preparation of WS₂ and MoS₂ nanotubes through a reaction of thin tungsten films or Mo₂O₃ with H₂S at elevated temperatures. The results have first implied that the materials possessing a layered structure, other than graphite, are indeed able to form energetically stable nanotubes under favorable growth conditions. During the last decade, various approaches were developed to synthesize a variety of layered tubes (composed of molecular layers), including $B_x C_y N_{z,3}^{-3}$ BN,⁴ NiCl₂,⁵ VO_{x,6} InS,⁷ MS₂ (*M*=Ti, Zr, Hf, Nb, and Ta),⁸ Bi,⁹ and ReS₂.¹⁰ Nowadays, these inorganic tubes with interesting properties and potential applications constitute an important domain of the nano- and microstructural family.

GaS, group III-VI semiconductor compound, is known to possess a layered structure, which consists of double layers of metal atoms sandwiched between double layers of nonmetal atoms, i.e., the layers contain four sheets of gallium and sulfur atoms stacked along the c axis in the sequence S-Ga-Ga-S, and there are two layers in the unit cell. The bonding between two adjacent layers is of the Van der Waals type, whereas the bonding within a layer is predominantly covalent.¹¹ Due to the layered nature of GaS, the existence of the stable tubular structure of this material has been predicted theoretically.¹² Very recently, Hu et al. reported the synthesis of GaS nanotubes by annealing the GaS lamellar precursor.¹³ Later Gautam et al. synthesized GaS nanotubes through a laser and thermally induced exfoliation method.¹⁴ Compared to the GaS bulk crystals, those synthesized GaS nanotubes have a low crystal quality, which would negatively affect their semiconducting performance in the real devices. Herein we report on the growth and optical properties of uniform and high-quality GaS submicrometer tubes synthesized via a simple high-temperature thermal reaction route.

The GaS submicrometer tubes were prepared in a vertical high-frequency induction furnace, which was described in detail elsewhere.¹⁵ A typical procedure was performed as follows: a graphite crucible containing a mixture of Ga_2O_3 , ZnS, and activated carbon powders was heated at high speed to 1400–1500 °C and kept at this temperature for 1.5 h, and then rapidly cooled to room temperature. The whole process was conducted in an Ar atmosphere under ambient pressure and a flow rate of 0.5–1.0 L/min.

After the synthesis, a C fiber thermo-insulating layer was densely covered with a greenish-yellow product. X-ray powder diffraction (XRD) spectrum, Fig. 1, conforms that assynthesized product contains only one crystalline phase, that is, hexagonal GaS [JCPDS (30-0576); a=3.587 Å and c=15.492 Å; space group: $P6_3/mmc$] with a layered structure. Scanning electron microscopy examination showed that the GaS products were straight tubes with lengths of up to \sim tens of micrometers.

Most of the tubes have uniform diameters and wall thicknesses throughout whole lengths, as shown in Fig. 2(a), in which this tube has a length of $\sim 90 \ \mu m$. Some tubes have outer diameters of ~600-900 nm and wall thicknesses of 200-300 nm [Fig. 2(b)]; the others have diameters of \sim 200–300 nm and wall thicknesses of \sim 60–100 nm [Fig. 2(c)]. In some cases, Fig. 2(d), the GaS tubes are partially filled with liquid metallic Ga "rods" [Ga may remain liquid (bulk Ga: mp of 29.8 °C) at lower T being confined with a nanotube];¹⁶ the Ga-filling occupies more than \sim 40–60% of the entire tube cavity. A small portion of the tubes has a very thick wall (\sim 300 nm in thickness) and a very narrow central channel (\sim 30 nm in diameter), as shown in Fig. 2(e). Most of the tubes appear to display open tip ends, as depicted in Fig. 2(f). Energy-dispersive x-ray spectroscopy revealed that the tubes consisted of gallium and sulfur in an atomic ratio 1:1; both the elemental map and spatially resolved elemental profile directly highlight a tubular geometry of the present GaS material (not shown).

Figure 3 shows high-resolution transmission electron microscopy (TEM) images and electronic diffraction (ED) patterns of a GaS tube with the outer and inner diameters of ~ 250 and ~ 80 nm, respectively. Figure 3(a) is the lattice

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FIG. 1. XRD spectrum of as-grown GaS layered crystals.

image of a GaS tube wall. As seen from the image, the wall is composed of regularly ordered molecular layers. Figure 3(b) displays an ED pattern taken from the wall. It resembles a double diffraction pattern, i.e., the electrons scattered by mutually parallel and very thin layers with the basal planes perpendicular to the electron beam-[001] zone partially overlap those scattered by the tube's longitudinal edge with the basal planes parallel to the beam-[010] zone. The strong {10*l*} diffraction spots of the [010] zone located at $l = \pm (2n)$ +1) do correspond to a hexagonal crystal. Figure 3(c) shows an ED pattern taken from a tube cavity, that can be indexed as the [001] zone axis of a GaS crystal. Figure 3(d) depicts a high-resolution TEM (HRTEM) image of the GaS layers whose (004) lattice fringes with a d spacing of 0.387 nm within the wall are parallel to the tube axis. Figure 3(e) is a HRTEM image taken from the cavity region. The image and the d spacing (~ 0.31 nm) well match those of a hexagonal GaS crystal viewed along the [001] zone axis; the Moiré fringes are due to the overlapping of the top and bottom



FIG. 2. TEM images of the GaS tubes. (a) Overall view of a tube (low magnification). (b) Larger and smaller (c) diameter uniform tubes. (d) A Ga-filled tube. (e) A tube with thick wall and narrow central channel. (f) An open-ended tube.



FIG. 3. HRTEM images and ED patterns of a GaS tube. (a) Overall lattice image of the tube wall. (b), (c) ED patterns taken from the tube wall and cavity, respectively. (d), (e) HRTEM images taken from the tube wall and cavity, respectively.

sidewalls of the tube. Further studies indicated that the axis direction, i.e., the growth direction of the tube, is parallel to the [120] crystallographic orientation of a GaS crystal, thus being perpendicular to the $\{100\}$ planes. Both the earlier TEM imaging and electron diffraction suggest that the tube grows through the successive rolling-up of molecular layers with the (001) basal plane, as observed in other layered structure tubes.¹⁷

From a chemical point of view, the formation of GaS tubes was accomplished through the decomposition of the source materials $(Ga_2O_3+2C \rightarrow Ga_2O+2CO, 2Ga_2O + 4CO \rightarrow 4Ga + C + 3CO_2$,¹⁸ $2ZnS \rightarrow 2Zn+S_2$, $2ZnS + C \rightarrow 2Zn+CS_2$ ¹⁹) followed by thermal reactions ($2Ga+S_2 \rightarrow 2GaS$, and $Ga_2O+CS_2 \rightarrow 2GaS+CO$) at a high temperature and in a carrying flow of pure Ar. Thus a very complex chemical process is suggested to take place. Though the details of a rolling-up mechanism accounted for the tube growth are not yet clear, we have observed the initial growth stage at thin GaS layers (or nanosheets) during TEM exami-



FIG. 4. TEM images showing a rolling-up mechanism for as-grown GaS tubes: (a) and (b) A rolling-up process along a GaS sheet's edge. (c) and (d) A microfold of a GaS sheet at the tube end, as marked with arrows.

nation. Figures 4(a) and 4(b) demonstrate thin GaS nanosheets; a bending and rolling-up process (indicated by arrows) along the edges results in the initial growth of a tube [therefore, TEM images and ED patterns are in agreement with those taken from a tube cavity (not shown)]. Figures 4(c) and 4(d) [magnified framed area of Fig. 4(c)] show a GaS tube whose tip-end domain can be considered to be a microfold (indicated by arrows) of a thin nanosheet. The observations are in accord with the reported growth process of MoS₂ nanotubes.² For a GaS nanotube (both zigzag and armchair types), based on density-functional tight-binding theory, it is proposed that GaS nanotube grows towards the value of two-dimensional hexagonal GaS sheet and is in contrast to carbon nanotube largely independent of the chirality.12 However, the detailed chemical process and growth mechanism of GaS submicrometer tubes require further systematic investigations.

Figure 5 shows a room temperature photoluminescence (PL) spectrum recorded from the synthesized GaS tubes. It is clear that two strong emission bands centered at \sim 585 nm (2.12 eV) and 615 nm (2.02 eV) are detected. The two bands are in agreement with the PL emission band (of \sim 656–539 nm, centered at \sim 582 nm) observed from the GaS bulk single crystals;²⁰ they probably are of impurity nature and are due to the radiative recombination of electrons



FIG. 5. Room temperature PL spectrum of as-synthesized GaS tubes.

from minimum of conduction band by holes from deep acceptor centers.^{20,21}

In conclusion, uniform GaS submicrometer tubes with layered structures have been synthesized via a simple hightemperature thermal reaction route. The cavities of these uniform GaS tubes may be further filled with different semiconducting materials of various band gaps leading to interesting electrical and optical nanodevices. In addition, theoretical predictions have indicated that GaS nanotubes exhibit a stable semiconducting gap,¹² independent of their chirality and converges rapidly with increasing diameter to that of the two-dimensional layer. The present results suggest that the designed simple method might be useful for the synthesis of other tubular structures made of group III–VI semiconductors in order to meet the growing demands of nano- and microscale science and technology.

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