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Template-free synthesis of helical hexagonal microtubes of indium nitride

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Single crystalline indium nitride (InN) helical microtubes with a hexagonal hollow cross section have been synthesized in bulk quantities by nitriding indium oxide powder in ammonia flux. As-prepared InN microtubes grow along the [0001] direction with typical outer diameters of 1–3 μm, wall thickness of 50–80 nm and lengths up to hundreds of microns. The InN microtubes exhibit both right-handed and left-handed helicities with helical angles ranging from zero to about 30°. Variation of helicity can be observed in a single tube. A number of observations demonstrate that the growth of the tubular structure occurs by the spiraling of the warped InN nanobelts. Photoluminescence spectrum of the microtubes presents a strong emission peak centered at 700 nm at room temperature. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2009841]

Indium nitride (InN) has been one of the focused issues in III-nitride semiconductors in the past couple of decades.[1] InN finds potential applications in many fields owing to its unique optical and electrical properties.[2–5] Studies on InN tubular structure are of benefit to understanding the topological or morphology-related effects to meet the increasing demand in micro-/nanotechnology. Only a few works[6–8] have been reported so far on InN tubular structure due to the synthesis difficulties such as low decomposition temperature and high equilibrium vapor pressures inherently possessed by the InN compound.[9,10] InN nano- and microtubes could be fabricated by solvothermal,[6] chemical vapor deposition (CVD),[7] and nitriding indium oxide (In_2O_3) in ammonia (NH_3) flux[8] approaches. The InN nanotubes prepared by CVD are nano scale in outer diameters and a few microns in lengths with square cross sections.[7] The InN microtubes synthesized by ammonolysis showed a hexagonal shape with the length up to few tens microns but with nonintact feature.[8]

In this letter, we report the fabrication of InN helical hexagonal microtubes by nitriding In_2O_3 powders in NH_3 flux. For inorganic tubular structures, helicity is a fundamental issue in layered nanotubes with chirality,[11,12] such as carbon,[13] boron nitride,[14] and metal disulfides,[15] but it is seldom observed in nonlayered tubular structures.[16,17] The helical morphology similar to our InN microtubes is found in the Ni–P amorphous alloy microtubes with irregular cross sections, which were molded from the helical-tape fibrous organic templates.[17] The present work, however, demonstrates that it is possible to grow helical semiconducting InN microtubes in bulk quantities without the presence of any templates. Moreover, both left- and right-handed helical motifs are observed in the products, and the two helicities can even simultaneously present in a single tube with a straight segment between them. A number of observations indicate that the InN microtubes are formed by spiraling of warped InN nanobelts.

Synthesis process was carried out by nitriding In_2O_3 powders in NH_3 flux in a conventional tube furnace.[8,18] The furnace was set at 953 K and 60 sccm NH_3 (anhydrous, 99.999%) was introduced into the tube during the whole reaction process. The exhaust ammonia was bubbled through a water reservoir before being discharged into the atmosphere. Fluey brown-gray product in bulk quantities was generated in the boat by controlled nitriding conditions. Phase identifications were carried out by x-ray powder diffraction (XRD) on a Rigaku D/max 2500 diffractometer with Cu $K\alpha$ radiation (45 kV, 250 mA). Morphologies and lattice fringes were imaged by a field emission scanning electron microscope [(SEM) HITACHI S-5200 and XL30 S-FEG] and a transmission electron microscope [(TEM) JEOL 2010, accelerating voltage of 200 kV]. Photoluminescence (PL) spectrum was recorded at room temperature on an Accent RPM2000 PL system using a 325.0 nm HeCd laser with power of 2.1 mW as the excitation light source.

Figure 1 shows typical morphologies and component analyses of the tubular product synthesized at 953 K for 30 h. SEM wide-field images shown in Fig. 1(a) reveal that the InN microtubes can be obtained in a high yield. These entangled microtubes have outer-diameters ranging from 1 to 3 μm and lengths of tens to hundreds of microns. Detailed investigation by SEM demonstrates that the morphology of the as-synthesized InN microtubes show uniform outer diameters along the tube axis and nonbranched morphology. The surfaces of the microtubes are smooth, well-faceted, and without any covering, as shown in Fig. 1(b). Figure 1(c) shows that these tubes possess hexagonal hollow cross sections with nanoscaled wall thickness of 50–80 nm. Most of the tubes are seamless and open at both ends with definite hexagonal frame, although a few holes can be found on the surfaces of some tubes. Electron energy-dispersive spectrometer (EDS) measurement demonstrates that the microtubes consist of only In and N, as evidenced in Fig. 1(d). According to XRD analysis shown in Fig. 1(e), there are no peaks of In_2O_3, which implies a high purity of the synthesized product. All of the peaks can be indexed by a hexagonal lattice with lattice constants of $a=3.546$ Å and $c=5.715$ Å, which agree well with the data on JCPDS card 50-1239 for wurtzite InN. TEM image in Fig. 1(f) manifests

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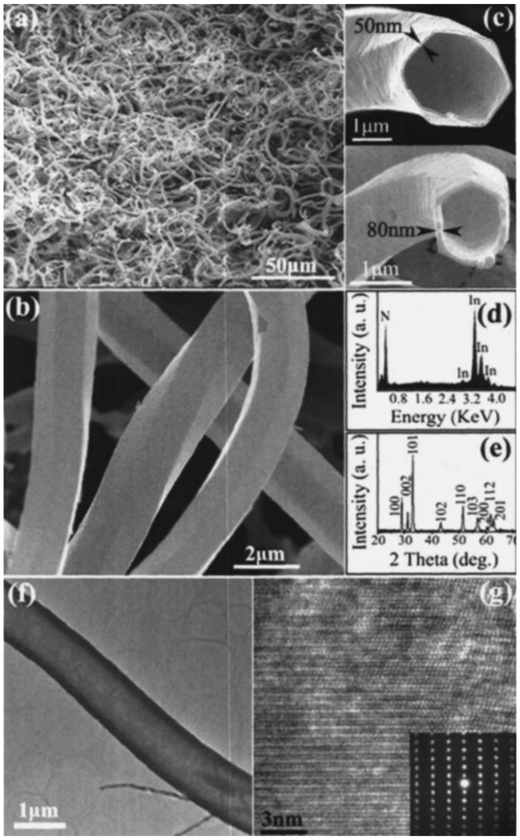

FIG. 1. (a) SEM wide-field image showing the entangled product. (b) High-magnification SEM image displaying the smooth surface. (c) Typical ends with an open hexagonal frame and wall thicknesses. (d) EDS spectrum of the as-synthesized product. (e) XRD spectrum demonstrating the wurtzite InN structure. (f) TEM image of a single microtube. (g) High-resolution TEM image obtained from a facet of a crushed microtube. Inset: SAED pattern corresponding to the image.

the center-hollow structure without any blockage in the whole microtube. High-resolution TEM image and selected area electron diffraction (SAED) obtained from a facet of a crushed microtube show that the microtubes are of good crystallinity and grow along the [0001] direction, as shown in Fig. 1(g).

Interesting helical configurations are observed on the microtubes shown in Fig. 2. Helical angle with respect to the tube axis is schematically indicated in the corresponding microtubes. Both right- and left-handed helicities exist clearly in our product with a wide distribution of helical angles ranging from zero (straight) to around 30° [Fig. 2(a)]. In particular, two types of helicities can even simultaneously exist in one individual microtube, as shown in Fig. 2(b). A segment of straight tube (Part B) connects the helical parts [Parts A and C in the inset of Fig. 2(b)] and acts as a buffer alleviating the deformation strain arising from the helicities.

Various experiments of nitriding In_2O_3 powders were carried out by adjusting reaction time while keeping other synthesis parameters unchanged. Different morphologies of the InN, such as nanowires,[18] nanobelts, and microtubes and so on, were achieved. According to SEM investigations, for example, there are pure nanobelts in the product obtained for a reaction time of 22 h [shown in Fig. 3(a)], while in the product for 26 h very few microtubes coexist with a large amount of nanobelts as shown in Fig. 3(b). Detailed SEM images provide more information regarding the epitaxial relation between nanobelts and microtubes, as shown in Figs. 3(c)–3(e). In the inset of Fig. 3(b) and Part C in Fig. 3(e), it is obvious that the nanobelts are bent in a direction vertical to the belt longitude into a warped shape. By increasing the reaction time, the morphology of InN evolves gradually from a flat nanobelt [Fig. 3(a)] to a warped nanobelt [Fig. 3(b)], a partially spiral microtube with integrant of hexagonal feature [Figs. 3(c) and 3(e)], and finally to a complete helical hexagonal microtube (shown in Figs. 1 and 2). Therefore, it is reasonable to propose that the formation of InN microtubes is related to the spiraling of InN nanobelts. The type of belt-rolled tube originated from spiral nanobelt counterpart is also reported on the preparations of tellurium and silica.[16,19] However, there are some differences between our observations and the formation model reported in Ref. 16 and Ref. 19. First, the spiraling of either a single nanobelt [Figs. 3(c) and 3(d)] or two nanobelts simultaneously [Fig. 3(e)] can result in the formation of tubular structure. Second, nano-

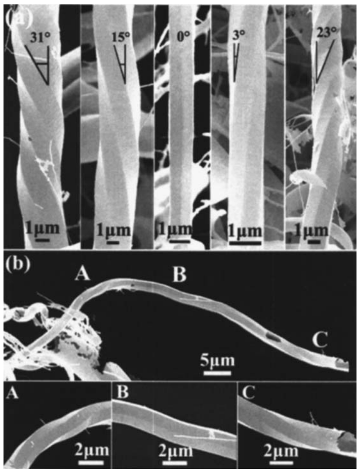

FIG. 2. Helical feature of InN microtubes. (a) Images displaying the microtubes in left- and right-handed helical configurations. Helical angles range from zero to around 30°. (b) A single tube with both left-handed (inset A) and right-handed (inset C) helical configurations, between which is a straight segment (inset B).

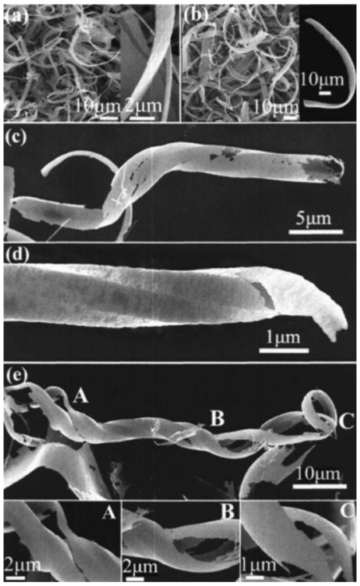

FIG. 3. (a) Beltlike product synthesized for 22 h. (b) Warped nanobelts with a few microtubes synthesized for 26 h. (c) and (d) Formation of microtubes by spirally winding of a single nanobelt. (e) Formation of a microtube by spirally winding of two nanobelts.

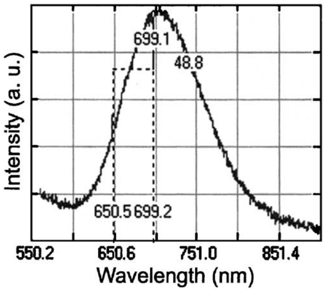

FIG. 4. PL spectrum of the synthesized microtubes.

belts are warped radially before forming the frame of a tube and even possess well-faceted morphology on the portion near to the resultant tube, as shown in the insets of Fig. 3(e). The joining between the neighboring side edges of the spiraled belts is likely completed through the decomposition-recombination process of InN compound via a vapor-solid mechanism, since the growth temperature is higher than the decomposition point (lower than 903 K) of InN.[9,10] Nevertheless, further studies would be necessary to understand the stacking strain, defects, transport motivity, dynamical and thermodynamic mechanism, etc.

A typical room-temperature PL spectrum is obtained from the synthesized helical InN microtubes, as shown in Fig. 4. In the range of 550–900 nm, a strong peak is manifested at around 700 nm which corresponds to an optical band gap of about 1.77 eV. Very scattered values between 0.65 and 2.2 eV have been reported for the band gap of InN.[1,6,7,20–22] The discrepancy of the reported values is considered to result from subtle difference in carrier concentrations, oxygen contamination, or defects of the samples.[1,6]

In summary, the InN helical microtubes were synthesized by nitriding In_2O_3 powder in flowing NH_3. The synthesized InN microtubes show hexagonal cross sections and helical feature. Both right- and left-handed helicities present in the product with the helical angle ranging from zero to about 30° and can even simultaneously exist in an individual microtube. The evolution of InN morphology from the nanobelts to the helical microtubes is demonstrated via the detailed SEM observations on the products prepared with different reaction time. The spiraling of either a single nanobelt or two nanobelts can result in the formation of the tubular structure. This new type of microtube is not only interesting for the fundamental research, but also potential as templates for constructing the one-dimensional helical structures applied in semiconducting nano/microdevices.

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