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Conformal conversion from helical hexagonal InN microtubes to In$_2$O$_3$ counterparts

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Cubic In$_2$O$_3$ microtubes were prepared by thermally oxidizing InN counterparts under controlled conditions. Similar to the starting InN sample, the converted In$_2$O$_3$ microtubes are hexagonal in cross section and exhibit helical motifs of both right-handed and left-handed architectures with helical angles of 0°–30°. InN microtubes can be retrieved by renitridation of the oxide microtubes. This work demonstrates that it is feasible to fabricate specific oxide nano-/microstructures from its corresponding nitride counterparts via controlled oxidation manner and vice versa. Temperature-dependent Raman scattering in both InN and In$_2$O$_3$ microtubes was measured and obvious downshifts of Raman modes were observed with increasing temperature. © 2006 American Institute of Physics. [DOI: 10.1063/1.2245438]

Indium oxide (In$_2$O$_3$) has been widely used in optoelectronics, solar cells, flat panel displays, and sensors due to its good electrical conductivity, optical transparency, and sensibility towards some gases.1,2 Currently, In$_2$O$_3$ structures at nano- or microscale have been extensively studied to provide functional components with reduced sizes.3,4 In comparison to the studies on nanobelts and wires/fibers,3,4 the investigations on tubular In$_2$O$_3$ are limited.5-7 Unique geometry associated with tubular structures would be advantageous for storage and transport of gases or liquid, which can hardly be performed by using thin film, solid wire, or particle counterparts.8

Tubular structures with complex morphologies are interesting for their potential applications related to the special shape. However, their growth is a formidable challenge and usually templates are employed.9,10 The tubular In$_2$O$_3$ structures are usually grown via vapor-phase5 or alumina template-directed approaches,6,7 exhibiting nanoscale outer diameters and round cross sections. We have previously grown InN microtubes by in situ nitriding In$_2$O$_3$ powders in ammonia (NH$_3$) flux and the as-prepared tubes shown hexagonal cross sections and helical architectures.11 In this letter, we report the fabrication of helical hexagonal microtubes of In$_2$O$_3$ by thermal oxidation of the InN counterparts in controlled conditions. This type of microtubes should not only be interesting for the fundamental research but should also have potential as templates for constructing the one-dimensional helical structures applied in semiconducting nano-/microdevices.

InN microtubes were synthesized by nitriding In$_2$O$_3$ powders in flowing ammonia, as described in a previous work.11 After loading the InN products, the open end of the quartz tube was connected to a mechanical pump. The oxidation temperature was set at 470 °C. The pump was turned on until the reaction tube was cooled down to room temperature. The spongy yellowy products after the reaction were characterized by using x-ray powder diffraction (XRD, Rigaku D’max 2500) and field-emission scanning electron microscopy (SEM, HITACHI S-5200). The x-ray photoelectron spectrum (XPS) was recorded on an MK II x-ray photoelectron spectrometer with an Al Kα x ray as the excitation source. Temperature-dependent Raman measurement was performed in backscattering geometry on a JY-HR800 micro-Raman system using a neodymium-doped yttrium aluminum garnet laser of 532 nm for excitation.

Figure 1 shows the XRD pattern of the product oxidized for 5 h (No. 2), comparing to that of the as-prepared InN microtubes (No. 1). All the strong diffraction peaks can be indexed to be body-centered cubic (bcc) phase with a lattice parameter of $a=1.015$ nm, in agreement with Joint Committee of Powder Diffraction Standards (JCPDS) Card No. 06-0416 (In$_2$O$_3$).12 It is noteworthy that the relative intensity of the peak (222) is a little enhanced in comparison with that of

\[ a = 1.015 \text{ nm} \]

![Graphical abstract](image)

**FIG. 1.** XRD patterns of the as-prepared InN (No. 1), converted In$_2$O$_3$ (No. 2), and renitrided InN (No. 3) microtube products.

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the standard in the card, suggesting a preferential orientation of the tubular products.

Figure 2(a) shows the presence of a large number of tubular structures which are mixed with a few nanobelts and nanowires. These entangled microtubes have outer diameters typically ranging from 1 to 3 \( \mu m \) and the maximum lengths of over 100 \( \mu m \). Detailed SEM investigation demonstrates that the morphology of the as-synthesized In\(_2\)O\(_3\) microtubes show a uniform outer diameter along the tube axis. Most of the tubes are seamless and open at both ends. Figures 2(b) and 2(c) show that these well-faceted tubes possess hexagonal cross sections with nanoscale wall thickness. The geometrical shape and sizes of the In\(_2\)O\(_3\) tubes are reminiscent of those of InN tubes. The SEM image at high magnification reveals that the oxide microtube is composed of nanoscale crystallites with grain sizes of 10–50 nm. Since the dissociation temperature of InN compound is \( \sim 550 ^\circ C \), higher than our treatment temperature, it is ruled out that the dissociation leads to the degraded crystal quality of the obtained oxide. We think that the formation of nanocrystallites in the obtained In\(_2\)O\(_3\) microtubes would be induced by the volume change from wurtzite InN to bcc In\(_2\)O\(_3\), although the geometrical shape of the product is almost unchanged.

As mentioned in the previous work, hexagonal InN microtubes show helical configurations. Considering that the converted In\(_2\)O\(_3\) microtubes “inherit” the fundamental geometry of the starting InN, it is reasonable to expect that In\(_2\)O\(_3\) products retain the helical configurations. Figure 3 exhibits the helical motifs of the oxide microtubes. Both left-handed [Figs. 3(a) and 3(b)] and right-handed [Figs. 3(d) and 3(e)] helicities are present. Extensive measurements on the tubes show that the helical angle varies from zero [namely, straight, as shown in Fig. 3(c)] to around 30°, well consistent with the helical angle range of the starting InN.

Thermodynamically, the oxidation reaction would be favorable because of the large difference of formation heat at 300 K between InN (-4.2 kcal/mol) and In\(_2\)O\(_3\) (-221.27 kcal/mol). A few studies have shown that oxygen is prone to incorporating into the InN by thermal treatments in the air or even during long-term storage at room temperature. The thermal oxidation of InN implies the change of In bonding partner from N to O, which is clearly indicated by XPS spectra shown in Fig. 4. For the starting InN microtubes, the O(1s) signal with a binding energy at around 531.6 eV corresponds to O absorbance on the surface of specimen. After the oxidation, N(1s) is lost almost completely whereas O is incorporated. The O(1s) peak shifts obviously to 529.7 eV which is associated with In–O bond. Correspondingly, the \( \text{In}(3d_{xy}) \) peak shifts slightly to a higher binding energy. Along with the bonding between In and O, the atoms are arranged to form cubic In\(_2\)O\(_3\) phase. It is noteworthy that the formed oxide crystal is preferred to orient in InN matrix with \( \text{In}_2\text{O}_3(222) \) paralleling to InN (0002). As for the synthetic strategy based on conformal conversion, the
shown on the right, respectively. Further nitridation of the In$_2$O$_3$ is not large enough to destroy the geometrical shape of the product, though it leads to the formation of nanocrystallites from InN to In$_2$O$_3$. The stress induced by the volume change must be considered. A volume increase is indicated by arrows in the room-temperature spectrum of the In$_2$O$_3$ product, as shown in Fig. 5(b). Similar to InN, with the increase of temperature both Raman modes shift downward by 7 cm$^{-1}$ for the former and 8 cm$^{-1}$ for the latter, respectively. In general, the effects of thermal expansion, strain, or anharmonic coupling to other phonons are considered to be the main factors causing the shift, as observed in many semiconductor thin films and nanostructures.

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FIG. 5. Raman spectra of InN (a) and In$_2$O$_3$ (b) microtubes as a function of temperature. Temperature-dependent Raman phonons of InN and In$_2$O$_3$ are shown on the right, respectively.

Volume difference must be considered. A volume increase is estimated to be 4.5% by XRD after the phase conversion from InN to In$_2$O$_3$. The stress induced by the volume change is not large enough to destroy the geometrical shape of the product, though it leads to the formation of nanocrystallites in the obtained In$_2$O$_3$ microtubes. Considering this fact, we anticipate a reversible conformal conversion between the nitride and oxide of indium. Further nitridation of the In$_2$O$_3$ microtubes was performed carefully, considering the kinetics of nitridation. The results show that the reaction is completed at 600 °C for 10 h, as evidenced from XRD analysis in Fig. 1 (No. 3). SEM imaging indicates that the obtained nitride still preserves the tubular shape and sizes similar to the starting InN microtubes. However, no clear facets along the tubes are presented. We infer that besides the volume shrink, the In loss is inevitable as suboxide In$_2$O vapor during the nitridation reaction, which leads to the porous and polycrystalline quality of the microtubes. Nevertheless, this strategy provides a feasible route for fabricating other specific InN nanostructures based on its oxide counterparts. Therefore, our results indicate that the nitride and oxide of indium can duplicate each other under a suitable controlled condition, preserving the originally topological characteristic of the counterparts.

Figure 5 shows the Raman spectra of the InN and In$_2$O$_3$ microtubes in the temperature range of 80–400 K, respectively. Lorentz model was used to fit the prominent Raman peaks. In the spectrum of InN at room temperature, the first-order modes of the prominent peaks correspond to the $A_1$ transverse optical (TO), high frequency $E_2$ ($E_2$(high)), and $A_1$ longitudinal optical (LO) at around 441, 489, and 580 cm$^{-1}$, respectively. As the temperature increases, all three modes clearly shift to lower wave numbers by about 14 cm$^{-1}$ for $A_1$(TO), 5 cm$^{-1}$ for $E_2$(high), and 18 cm$^{-1}$ for $A_1$(LO), respectively. In contrast, two modes can be found at about 300 and 495 cm$^{-1}$ (indicated by arrows) in the room-temperature spectrum of the In$_2$O$_3$ product, as shown in Fig. 5(b).

12ICPDS Card No. 06-0416 (ICDD, 1998).