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Vapor–solid growth route to single-crystalline indium nitride nanowires

Jun Zhang,*[a,b] Lide Zhang,[a] Xinsheng Peng[a] and Xiangfeng Wang[a]

[a] *Institute of Solid State Physics, Chinese Academy of Sciences, PO Box 1129, Hefei 230031, PR China*
[b] *Department of Physics, Yantai University, Yantai 264005, PR China. E-mail: jzhang@ytu.edu.cn; Fax: +86-535-6903201; Tel: +86-535-6902146*

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Large-scale fabrication of hexagonal wurtzite structure single-crystalline indium nitride nanowires was achieved through a gas reaction from mixtures of In metal and In_2O_3 powders with flowing ammonia at 700 °C *via* a vapor–solid process.

The fabrication of nanometre-scale one-dimensional structure (nanotubes and nanowires) materials has attracted considerable efforts due to the potential utilization of the materials in both fundamental physical research and the future development of nanodevices.[1] The wide bandgap, group III nitride semiconductors (Al, Ga, In)N are currently the subject of much interest both for investigation of their fundamental physical properties and for their potential as high-temperature electronic and visible/near-UV optoelectronic devices. However, InN has not received as much experimental attention as GaN[2–9] due to difficulties associated with the growth of high quality crystals. Because InN has promising transport and optical properties and its large drift velocity at room temperature could render it better than GaAs and GaN for field effect transistors,[10] an understanding of the optical and structural properties of InN will advance the development of light-emitting group III nitride devices. Until very recently, only one group has reported InN nanowires from an azido-indium precursor based on the vapor–liquid–solid (VLS) process.[11] However, no report of large-scale fabrication of InN nanowires based on the vapor–solid (VS) process has been made so far. Herein we report a novel method for synthesizing InN nanowires. Based on the VS process, using mixtures of In metal and In_2O_3 powders with flowing ammonia in 700 °C horizontal oven, we have synthesized single-crystalline InN nanowires.

Firstly, an Al_2O_3 membrane was used as a substrate for growth of InN nanowires. The substrate was rinsed with deionized water before use. Secondly, a mixture of 2 g high purity In metal (purity 99.999%) and 1.21 g In_2O_3 (mole ratio 4 : 1), which were used as the starting materials, was placed in an alumina crucible. The crucible was placed in the hot zone inside a long quartz tube. The quartz tube was degassed under vacuum and purged with ammonia. The temperature of the crucible was increased to 700 °C from room temperature and kept at 700 °C for 2 hours under a constant flow of ammonia. Ammonia was introduced into the quartz tube through a mass-flow controller at rates of 400 standard cubic centimetres per minute (sccm). Finally, the quartz tube was quickly cooled down with the NH_3 flowed turned off. A light-yellow layer formed on the substrate.

The morphology and structure of the as-prepared products were characterized by X-ray diffraction (XRD, Philips PW 1710 with Cu Kα radiation), scanning electron microscopy (SEM, JOEL JSM-6300), transmission electron microscopy (TEM, JEM-200CX), high-resolution transmission electron microscopy (HRTEM, JEOL-2010) and energy dispersive X-ray spectroscopy (EDS) (EDAX, DX-4 attached to the JEOL-2010).

A typical SEM image in Fig. 1(a) shows that the material resulting from the reaction of the mixture of In and In_2O_3 with ammonia produced a high yield of nanometre wire-like structures. The high-magnification SEM image shows the nanowires are straight and smooth on their surfaces. The InN nanowires have diameters of 10–100 nm and a maximum length of several hundred micrometres.

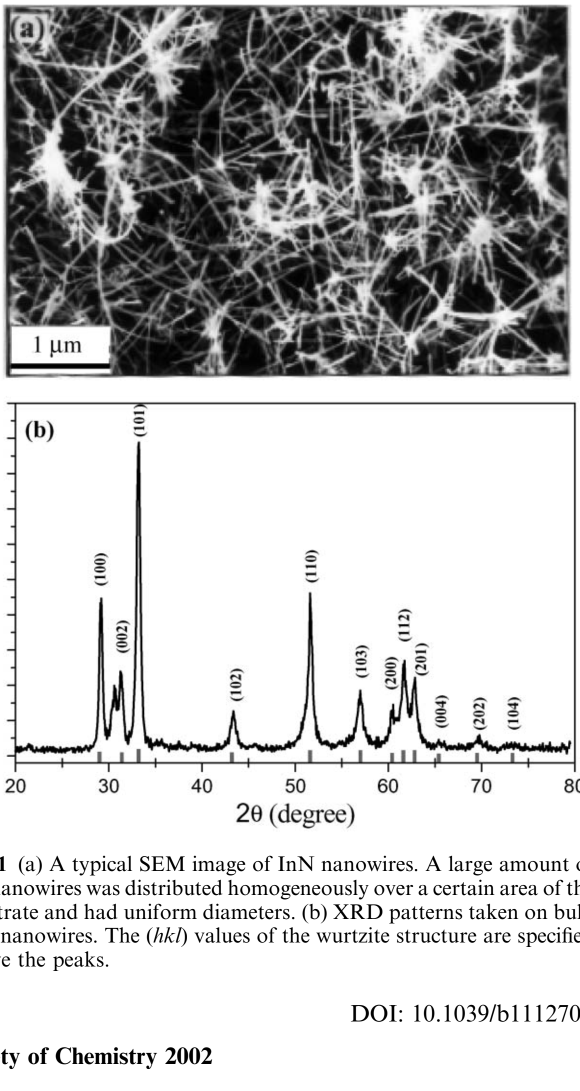

Fig. 1 (a) A typical SEM image of InN nanowires. A large amount of the nanowires was distributed homogeneously over a certain area of the substrate and had uniform diameters. (b) XRD patterns taken on bulk InN nanowires. The (*hkl*) values of the wurtzite structure are specified above the peaks.

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Fig. 1(b) shows the XRD pattern of the sample. All the reflections in the figure can be indexed to be a pure hexagonal wurtzite phase InN (Miller indices are indicated on each diffraction peak) with a lattice parameter $a_o = 3.52$ Å, $c_o = 5.71$ Å, which agree well with the reported values of InN bulk crystals (JCPDS 2-1450). The strong intensities of the InN diffraction peaks indicated that the resulting product had high purity of the InN hexagonal wurtzite phase.

The structural and elemental analyses of an individual InN nanowire were performed using TEM and EDS. The results reveal that the InN nanowires have diameters of 10–100 nm and lengths up to several hundred micrometres. A typical TEM image in Fig. 2(a) showed that the InN nanowire was smooth and straight, and the average diameter of an individual InN nanowire was 40 nm. Fig. 2(b) shows the high-magnification TEM image of the end of the InN nanowire; no particle was observed at the ends of the nanowires in our observations.

The HRTEM image in Fig. 2(c) of the InN nanowire shows the clear lattice fringes, and indicates a single-crystalline structure of the nanowire. In this image, the space of about 0.285 nm between arrow-heads corresponds to the distance between (002) planes and an arrow indicates the growth direction of the nanowire. The inset at the right-hand bottom of the image is a selected area electron diffraction pattern (SEAD) of the nanowire. The electron diffraction patterns were indexed to the reflection of the hexagonal InN crystal, which was consistent with XRD measurement of InN nanowires. The electron diffraction pattern indicates that the nanowire grows along [001] and it is enclosed by ±(001) and ±(010) crystallographic facets. So the observations from the electron diffraction patterns and HRTEM analyses together reveal further that the InN nanowire is single-crystalline. The EDS spectrum shown in Fig. 3 of the individual InN nanowire indicated that the nanowire consisted of In and N; the molecular ratio of In : N of the nanowire calculated from the EDS data was close to that of a bulk InN crystal. The Cu signals are generated from the microgrid mesh that supports the nanowires.

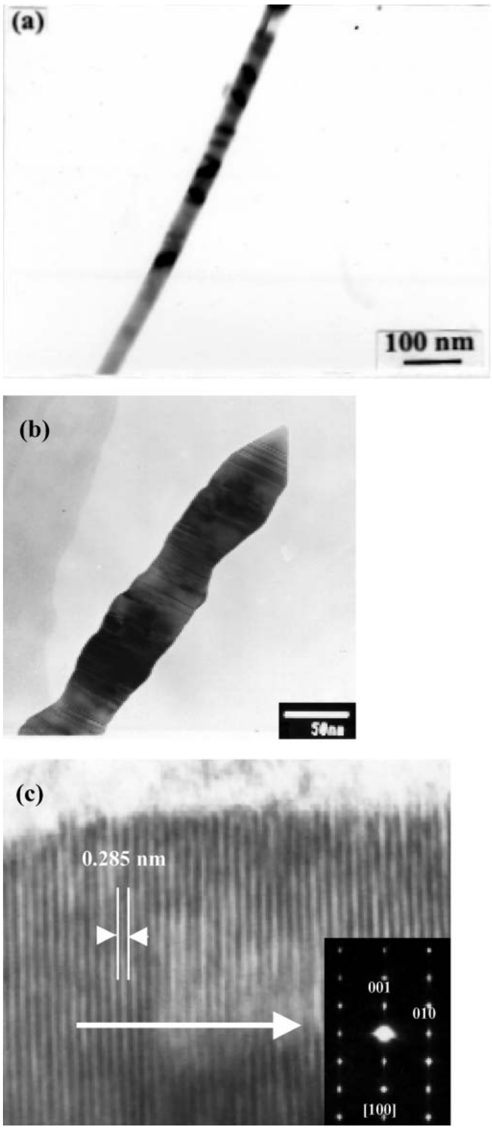

Fig. 2 (a) A typical TEM image of an individual InN nanowire. The image shows the nanowire with a uniform diameter. (b) A typical high-magnification TEM image of the end of the InN nanowire. (c) HRTEM image of an InN nanowire, showing a clean and structurally perfect surface. In this image, an arrow indicates the growth direction [001] of the nanowire. The space of about 0.285 nm between arrow-heads corresponds to the distance between (002) planes. The inset at the right-hand bottom of the image is the SEAD patterns of the nanowire. The nanowire grows along [001] and it is enclosed by ±(001) and ±(010) crystallographic facets.

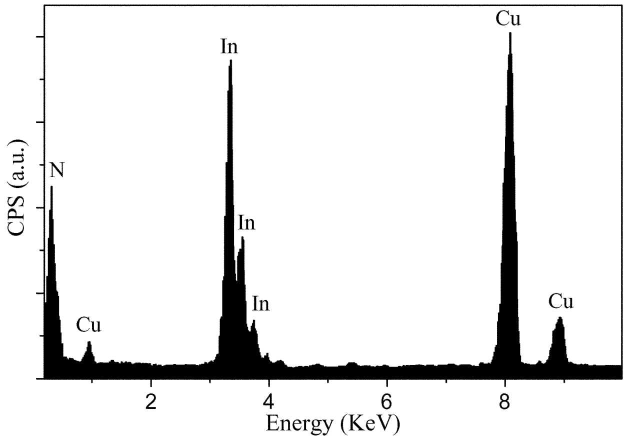

Fig. 3 EDS of an individual InN nanowire. The Cu signals are generated from the microgrid mesh that supports the nanowires.

Further evidence for the formation of InN can be obtained from the X-ray photoelectron spectra (XPS) of the product. The XPS was recorded on a VGESCALAB MKII X-ray Photoelectron Spectrometer, using non-monochromatized Mg Kα X-ray as the excitation source, and the In(3d) and N(1s) core level regions were examined. Fig. 4 shows the XPS spectra of the sample. The two strong peaks at 396.1 and 443.6 eV correspond to the N(1s) and In(3d) binding energy, respectively, for the InN. No obvious peak for indium oxide (444.9 eV for In3d5/2 in In_2O_3 and 445.0 eV in $In(OH)_3$) is observed. The ratio of the quantification of peaks N : In is close to 1 : 1, which is consistent with that found by elemental analysis.

Data from SEM, TEM and HRTEM analyses together reveal that the growth of the InN nanowires may not be dominated by the vapor–liquid–solid (VLS) process[12–14] proposed for the nanowires grown by a catalysis-assisted technique.[9–11] In the VLS growth process, a metal particle is located at the growth front of the wire and acts as the catalytically active site. In the present work, no metal catalyst is used, and no particle was observed at the ends of the nanowires in our observations [shown in Fig. 2(b)]. InN directly deposits on the substrate at a lower temperature region and grows into wire-like nanostructures. Therefore, it is likely that the growth is governed by a VS process.[15]

In conclusion, a novel non-catalytic synthesis route to crystalline InN nanowires has been developed. The reaction conditions in our route are very easy to maintain. Large-scale synthesis of InN nanowires was achieved from a mixture of In and In_2O_3 with a constant flowing ammonia atmosphere. XRD and TEM observations demonstrated that the InN nanowires were single-crystalline. The XPS spectrum of InN

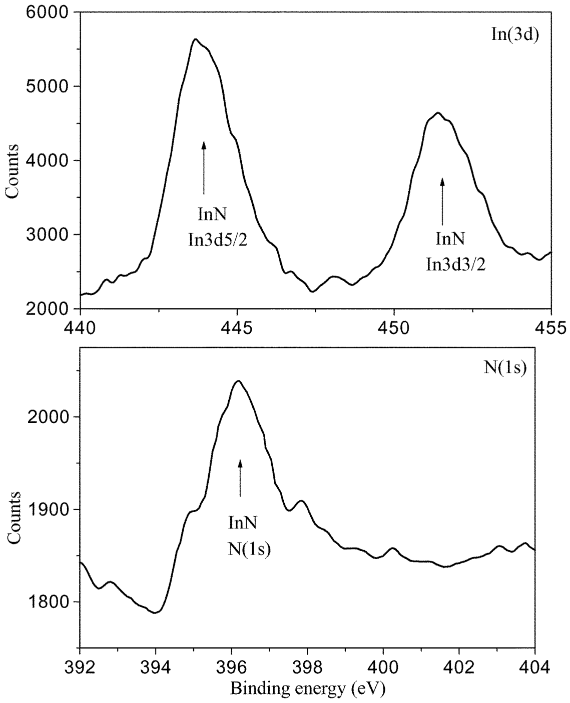

Fig. 4 XPS spectra of the InN nanowires.

nanowires was reported. The nanowires were 10–100 nm in diameter and up to several hundred micrometres in length.

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