

Growth and morphology of 0.80 eV photoemitting indium nitride nanowires

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InN nanowires with high efficiency photoluminescence emission at 0.80 eV are reported. InN nanowires were synthesized via a vapor solid growth mechanism from high purity indium metal and ammonia. The products consist of only hexagonal wurtzite phase InN. Scanning electron microscopy showed wires with diameters of 50–100 nm and having fairly smooth morphologies. High-resolution transmission electron microscopy revealed high quality, single crystal InN nanowires which grew in the $\langle 0001 \rangle$ direction. © 2004 American Institute of Physics.
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The group-III nitrides have become an extremely important technological material over the past decade.¹ They are commonly used in optoelectronic devices, such as high brightness light-emitting diodes² and low wavelength laser diodes³ (LDs), as well as high power/high frequency electronic devices.^{4,5} Recently InN thin films grown by MOCVD and MBE were found to have a band-gap energy in the range of 0.7–0.9 eV,^{6–8} much lower than the value of ~ 1.9 eV found for InN films grown by sputtering.⁹ This large decrease in the direct band-gap transition energy and the ability to form ternary (InGaN) and quaternary (AlInGaN) alloys increases the versatility of group-III nitride optoelectronic devices, ranging from the near IR to the UV. Additionally, InN has some promising transport and electronic properties. It has the smallest effective electron mass of all the group-III nitrides, which leads to high mobility and high saturation velocity,¹⁰ and a large drift velocity at room temperature.^{4,5,11} As a result of these properties, there has been a large increase in interest in InN for potential use in optoelectronic devices, such as LDs and high efficiency solar cells, as well as high frequency/high power electronic devices.

Unfortunately, high quality InN is very difficult to synthesize. It has a very low decomposition temperature and requires a large overpressure of N. There are only a few reports on thin film deposition of InN^{12–17} and on the one-dimensional synthesis of InN nanostructures. Vapor–solid growth of InN nanowires using a mixture of In metal/In₂O₃ powder and ammonia has been reported.¹⁸ Other InN nanostructure synthesis methods use a solvo-thermal method,¹⁹ halide chemical vapor deposition (CVD),²⁰ CVD using single-source precursors N₃In[(CH₂)₃NMe₂]₂,²¹ and ammonolysis of indium oxide.²² There are also reports on the synthesis of more advanced structures such as InN/InP core/sheath nanowires²³ and InN/GaN nanoheterojunctions²⁴ as well as the catalytic selective area growth on gold patterned Si(100) substrates.²⁵ The wires obtained by this catalytic growth technique exhibit a broad photoluminescence (PL) at

1.85 eV. In this letter, we report the synthesis of single crystal, 0.80 eV photo-emitting InN nanowires using In metal and ammonia. The InN nanostructures are formed using a vapor solid growth mechanism deposited on both the quartz surface and the In source metal surface.

The growth of InN nanowires was performed in a high temperature tube furnace with a quartz tube. High purity In metal (99.999%) was placed in a quartz boat in contact with a thermocouple to assure accurate growth temperature measurement. High purity ammonia (5N) flowed at 200 sccm for 1 h while the temperature was being ramped to a final growth temperature of 700 °C. The furnace was held constant at this temperature while ammonia was flowed over the quartz boat at 600 sccm for 2 h. The samples were rapidly cooled down to room temperature under ammonia flow before being purged with N₂. The samples were collected from both the surface of the In metal and from the surface of the quartz boat up to 2 cm downstream of the In source metal. Structural and compositional characterization were performed using powder x-ray diffraction (XRD) (Bruker D-8 GADDS) with a Co K α x-ray source, scanning electron microscopy (SEM) using a FEI Sirion 75 microscope equipped with an electron energy-dispersive spectrometer (EDS), and high resolution transmission electron microscopy (TEM) using a JEOL 2011 capable of selective area electron diffraction and nanobeam electron diffraction (NBD). Optical characterization was performed using room-temperature PL. The PL signals were generated in the backscattering geometry by excitation with the 515 nm line of an argon laser. The emission signals were dispersed by a 1 m double-grating monochromator and detected by a LN₂ cooled Ge detector.

Figure 1(a) shows a typical SEM image of InN nanowires taken from the surface of the quartz boat. Typical nanowire diameters were in the range of 50–100 nm with typical lengths of several microns. The surface morphology of the nanowire as shown in the inset of Fig. 1(a) appears smoother than the morphologies of wires obtained from other growth strategies for InN.^{18,23} Figure 1(b) shows the corresponding EDS spectrum for an individual nanowire indicating that the nanowires consist of In and N in an atomic ratio of approximately 1:1. These results were reproducible

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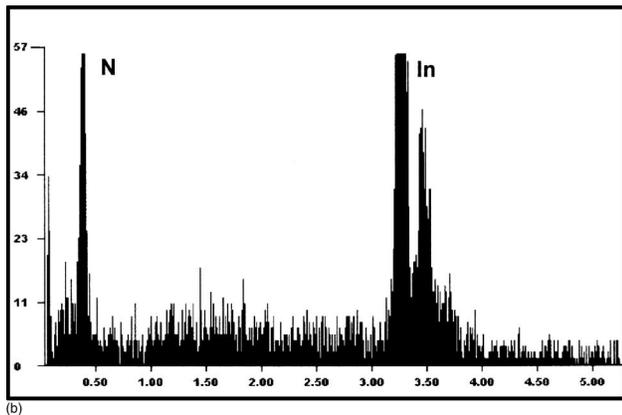
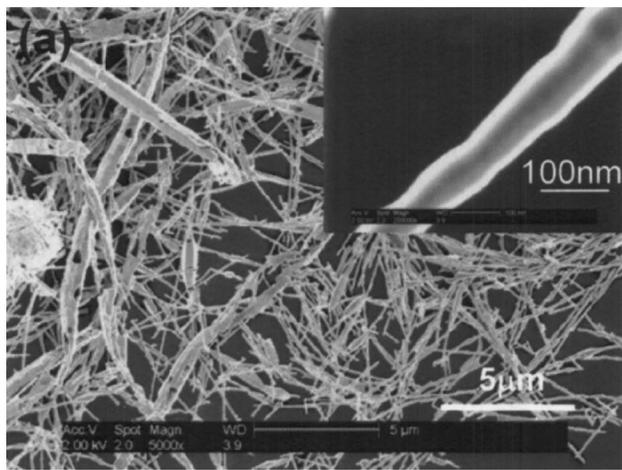


FIG. 1. (a) Typical SEM image of InN nanowires. The diameters of the wires range from 50 to 100 nm with some thick InN ribbons. The inset is a typical high magnification image of a single InN nanowire. (b) EDS of a single InN nanowire show that the resulting wires are pure InN.

over many growth runs which show that this technique is capable of synthesizing InN nanowires with uniform compositions.

Figure 2 shows the XRD pattern for InN nanowires. All the diffraction peaks in the spectrum are indexed to be hexagonal wurtzite phase. The lattice parameters were calculated

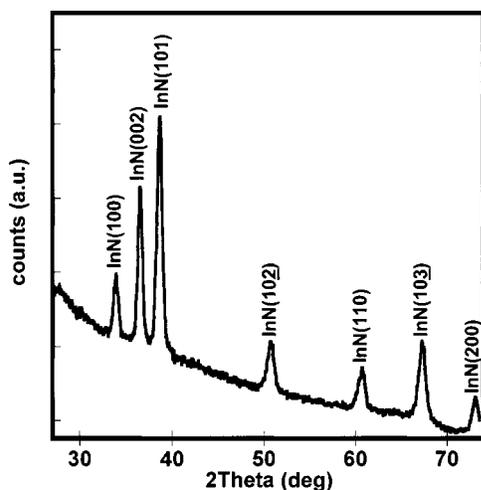


FIG. 2. XRD spectrum for InN nanowires grown at 700 °C using indium metal and ammonia. InN nanowires consist of only the hexagonal wurtzite phase with the corresponding indices marked above the respective diffraction peak.

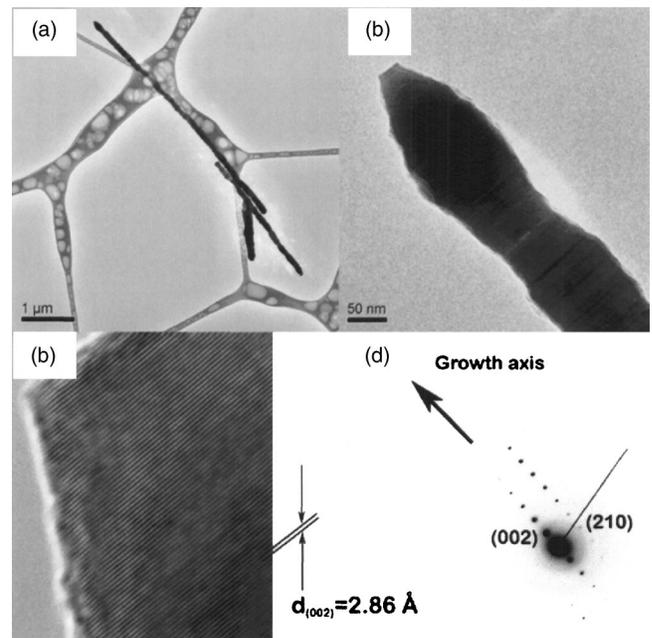


FIG. 3. (a) Typical TEM image of an individual InN nanowire. (b) High magnification TEM image of InN nanowire. Nanowires have a diameter that fluctuates between 50 and 100 nm. (c) High resolution TEM image of InN nanowire showing lattice spacing of the (002) planes to be 0.286 nm. (d) Nanobeam electron diffraction of InN nanowire.

to be $a=3.52 \text{ \AA}$ and $c=5.71 \text{ \AA}$, which are in good agreement with the reported values of bulk InN. The strong intensities of the InN diffracted peaks and the absence of any indium oxide peaks indicate that the InN nanowires are of high purity and the sample consists of only wurtzite phase material.

HRTEM study unravels more detailed structural and morphological information. Figures 3(a) and 3(b) show a typical InN nanowire. Although the diameter fluctuates by about 30% along the nanowire, we find that the wire is monolithic single crystalline material growing in the (0001) direction. Figure 3(c) displays the high quality of the nanowire showing the (0002) planes perpendicular to the wire axis with an interlattice spacing of 0.286 nm. Figure 3(d) shows the NBD patterns where the unit cell constants are measured to be $a=3.50 \text{ \AA}$ and $c=5.70 \text{ \AA}$, which are in good agreement with the measurements from XRD studies.

These wires grew directly on the quartz boat with no intentional catalysts present indicating that the growth mechanism was governed by a vapor–solid process. Further optimization of the growth parameters should allow growth of smoother and thinner wires.

Figure 4 shows the room-temperature PL spectrum for as-grown InN nanowires. The PL peak emission is located at 0.80 eV, which is consistent with literature results reporting a band-gap energy emission in the range of 0.70–0.90 eV.^{6–8} More importantly, the emission was extremely intense relative to the amount of material produced and the low incident laser power used (9 mW) although a quantum efficiency cannot be determined from these measurements at this time. The PL emission from these nanowires was compared to high quality thin films grown using (MOCVD)¹² as shown in Fig. 4. It is clear that these single crystalline nanowires have a very similar emission spectrum but with a narrower full width at half maximum indicating a higher quality material. Additionally, the peak emission is redshifted by 30 meV, which indicates a lower band-gap energy than the thin film.

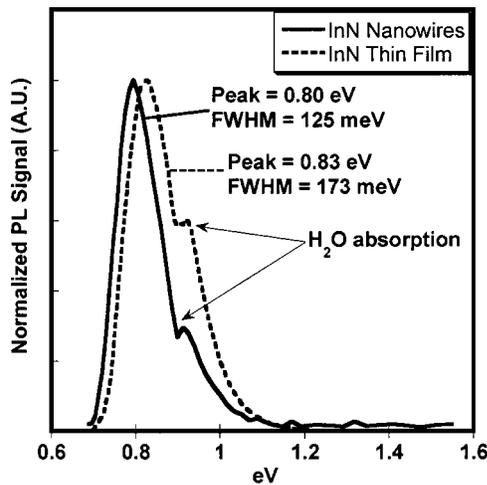


FIG. 4. Room-temperature PL of bulk InN nanowires compared to MOCVD grown InN thin film. The peak emission energy of the nanowires is 0.80 eV.

These PL results show the possibility of determining fundamental properties of InN from nanosize material eliminating many of the dislocations and impurities inherent to thin film materials. More detailed studies of the optical and transport properties of these InN nanowires are being investigated.

In conclusion, we have developed a simple and reproducible method by which we can synthesize InN nanowires with a vapor–solid growth process using In metal and ammonia as the reactant species. SEM and EDS show that the wires range between 50 and 100 nm in diameter with lengths up to several microns and consist of high purity InN. TEM results show that the wires are single crystal growing in the $\langle 0001 \rangle$. The PL emission is highly efficient with a peak emission energy at 0.80 eV. The growth mechanism is still being investigated but this simple technique appears promising for developing high efficiency InN-based nanosize optoelectronic devices.

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