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H. Y. Xu, Z. Liu, X. T. Zhang, and S. K. Hark

Letters

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Synthesis and optical properties of InN nanowires and nanotubes

H. Y. Xu, Z. Liu, X. T. Zhang, and S. K. Hark^{a)}

Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong

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InN nanowires and faceted hexagonal InN nanotubes are synthesized by catalyst-free chemical vapor deposition at different temperatures. Both have the single crystalline wurtzite structure and grow along the *c* axis. Different growth dynamics are suggested for the difference in morphology. Observations of phonon-plasmon coupled modes in their Raman scattering suggest of high electron concentrations. Absorption edges in their optical spectra have energies slightly higher than 1 eV, showing blueshifts from the fundamental band gap of ~0.7 eV, recently observed in epitaxial films. The shifts are argued to be the result of the Burstein-Moss effect. © 2007 American Institute of Physics. [DOI: 10.1063/1.2712801]

Indium nitride (InN) is currently receiving much attention, in large part due to its recently observed narrow band gap of ~0.7 eV.¹⁻³ This implies that light emitting diodes based on group-III nitride alloys such as (Al, Ga, In)N can cover a wide spectral range from ultraviolet (~6.2 eV) to near infrared (~0.7 eV). In addition, InN has superior electron transport properties, including high mobility and high saturation velocity at room temperature, which make it suitable for many optoelectronic applications, such as highspeed field-effect transistors, terahertz emitters, and highefficiency solar cells.

In recent years, one-dimensional (1D) semiconductor nanomaterials have become a subject of intense research, because of their importance in the understanding of the fundamental properties of low dimensional systems, as well as in potential nanodevice applications. Among group-III nitrides, 1D GaN and AlN nanostructures have been extensively studied.^{4,5} In contrast, the synthesis of high quality InN is still challenging, due to its low thermal decomposition temperature and the high equilibrium vapor pressure of nitrogen. Thus, reports on 1D InN nanomaterials, $^{6-13}$ especially those with a tubular structure, $^{14-17}$ are very limited. Chemical vapor deposition (CVD) has proven to be a feasible method to prepare InN nanomaterials. However, it is observed, in most available reports on CVD-grown InN, that In₂O₃ is usually contained in the precursors,^{7,8,14-16} which may lead to oxygen contamination and increased band gap of the resultant InN.^{18,19} In this work, InN nanowires and faceted hexagonal InN nanotubes are prepared from high purity In metal and ammonia by controlled normal pressure CVD without catalysts and templates. Their optical properties are investigated.

High purity indium wires (99.999%), serving as the starting material, were placed in a quartz boat. Prior to each experiment, the indium wires were cleaned using dilute hydrochloric acid and de-ionized water to remove any native oxide layer present on their surface. The quartz boat was loaded into the center of a 15 mm diameter quartz tube, which was placed in a horizontal tube furnace. The quartz tube was degassed and then purged with high purity ammonia. During the growth process, the flow rate of ammonia was set at 30 SCCM (SCCM denotes cubic centimeter per

minute at STP), and the furnace was maintained at 800 or $850 \,^{\circ}$ C for 200 min. Finally, the tube and its contents were rapidly cooled down to room temperature, all the time under the protective flow of ammonia, by removing them from the furnace, which suppressed the decomposition of the synthesized InN. Fluffy products were collected from the downstream side of the starting materials.

The morphologies, structures, and compositions of the synthesized products were characterized by scanning electron microscopy (SEM) (LEO 1450VP), high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai 20), x-ray diffraction (XRD) (Rigaku RU-300 with Cu $K\alpha$ radiation), and energy-dispersive x-ray (EDX) microanalysis. Optical transmission measurements were performed using a spectrophotometer (Hitachi U3501) on InN nanostructures dispersed in ethanol. Raman scattering was measured by a micro-Raman spectrometer (Renishaw RM1000B) in a back-scattering configuration, employing the 514.5 nm line of an Ar⁺ laser as the excitation source.

XRD measurements on the samples synthesized at 800 and 850 °C show that all diffraction peaks can be indexed to wurtzite InN, suggesting the formation of high purity InN material.

Figure 1(a) shows a typical SEM image of the sample synthesized at 800 °C, which consists of a high density of InN nanowires. The nanowires have an average diameter of \sim 100 nm with a narrow size distribution, and lengths up to a few tens of microns. When the temperature increases to 850 °C, the synthesized product contains a large amount of InN nanotubes and a fraction of nanowires, as shown in Fig. 1(b). The nanotubes are well faceted with a hexagonal cross section, about 750-1050 nm in outer diameter, and several microns in length. The wall thicknesses are in the range of 50-100 nm. Most of the nanotubes have both ends open. The microstructures and morphologies of InN nanostructures were further studied by HRTEM and selected area electron diffraction (SAED). The inset in Fig. 2(a) shows a SAED pattern of a single nanowire along the [100] zone axis, which confirms that the synthesized InN nanowires are single crystalline with a [001] growth direction. The HRTEM image of the nanowires in Fig. 2(b) shows clearly the lattice fringes with interplanar spacings of 0.57 and 0.31 nm corresponding to the (001) and (100) planes of wurtzite InN. Figure 2(c)displays a typical TEM image of an InN nanotube. The tube wall is smooth. The obvious contrast between the wall and

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^{a)}Author to whom correspondence should be addressed; electronic mail: skhark@phy.cuhk.edu.hk



FIG. 1. SEM images of InN (a) nanowires and (b) nanotubes. A high magnification SEM image in the inset clearly shows an InN nanotube of hexagonal cross section.

the core region again confirms the hollow nature of the tube. The SAED pattern indicates that the faceted hexagonal InN single crystalline tubes grow along the [001] direction, and are enclosed by low-index {100} planes. This observation differs from that reported by Yin *et al.*¹⁶ EDX spectrum in Fig. 2(d) illustrates that the synthesized products consist of



FIG. 2. TEM images of a single InN (a) nanowire and (c) nanotube. The insets in (a) and (c) show their SAED patterns along the [100] zone axis. (b) A HRTEM lattice image of a typical InN nanowire. (d) EDX spectra of a single InN nanowire and nanotube.



FIG. 3. Micro-Raman spectra of InN nanowires and nanotubes.

only In and N elements. The Cu signals come from the TEM grid. Quantitative analyses determine the In/N atomic ratios as 48.3:51.7 and 47.9:52.1 for the individual wires and tubes, respectively, which are stoichiometric, within experimental errors.

It has been observed that both InN nanowires and nanotubes grow along the [001] direction. As is known, there is no center of inversion in the wurtzite structure, and therefore, the presence of an inherent asymmetry along the *c* axis allows the anisotropic crystal growth along the [001] direction.^{5,20} In the present work, neither a catalyst nor a template is used, and no metallic particles are found at the ends of 1D InN nanostructures. Thus, the growths of InN wires and tubes are likely to follow a vapor-solid (VS) process. It is interesting to note that the morphologies of the synthesized InN 1D nanostructures depend on the growth temperatures. This can be understood by considering the kinetics-limited and diffusion-limited processes. Similar mechanism has been proposed in Refs. 16, 20, and 21 to understand the nanowire and nanotube growths of different materials.

Figure 3 gives the micro-Raman spectra of InN nanowires and nanotubes. Both show analogous features. The peak at ~443 cm⁻¹ corresponds to the A_1 transverse optical mode of wurtzite InN. The E_2 (high) modes are observed at 488 and 493 cm⁻¹ for InN wires and tubes, respectively. It is known that the E_2 (high) mode is especially sensitive to lattice strain. The strain-free Raman frequency of the E_2 (high) mode has been reported to be 490 cm⁻¹ for wurtzite InN.²² The E_2 (high) mode frequencies observed in our experiment are very close to this reported value, within an instrumental error of 2.5 cm⁻¹, which indicates that the strain of the synthesized InN nanostructures is fully relaxed. The Raman peak at ~570 cm⁻¹, which shows a redshift relative to the A_1 longitudinal optical (LO) mode reported at 585-590 cm⁻¹,²³ may be attributed to the lower branch of the large-wave vector $A_1(LO)$ -phonon-plasmon $(A_1$ -LPP⁻) coupled mode.²⁴ This coupled mode has also been observed in GaAs and InN films of high carrier concentrations.^{24,25} The presence of A_1 -LPP⁻ mode, along with the broad feature of the Raman peaks, suggests that the synthesized InN nanomaterials have high electron concentrations,^{23,24,26} mainly due to the contribution of native donor defects such as N vacancies and/or dislocations.

Figure 4 shows the optical transmission spectra of the synthesized 1D InN nanostructures dispersed in ethanol. The transmittances of both samples start to decrease at around 0.9 eV. The optical band gap can be estimated by plotting



FIG. 4. Optical transmission spectra of InN nanostructures dispersed in ethanol. The inset is the corresponding plots of $[\ln(1/T)]^2$ vs $h\nu$.

 $[\ln(1/T)]^2$ vs $h\nu$ (photon energy) and extrapolating the linear portion to $[\ln(1/T)]^2 = 0$. Using this method, the optical band gaps of the samples synthesized at 800 and 850 °C are determined to be 1.26 and 1.05 eV, respectively. The fundamental band gap of InN is a controversial issue. The inconsistent values which vary over a large range from ~ 0.7 to \sim 2.0 eV have been reported. Various mechanisms have also been proposed to explain the band gap differences in InN, such as the incorporation of oxygen, the Burstein-Moss effect, the quantum confinement effect, the strain effect, Mie resonance, and the nonstoichiometry.^{12,18,19,26–28} The optical band gaps of our InN nanostructures show a clear blueshift relative to the values of 0.7-1.0 eV, which are now generally accepted as the band gap of InN by many researchers. Possible reasons are discussed as follows: (1) EDX analyses indicate the high purity of the synthesized products, which excludes the effect of oxygen impurity on the band gap. (2) The theoretical calculations have shown that the quantum confinement effect is significant for nano-InN with sizes less than 20 nm.¹² However, the sizes of our InN nanowires and nanotubes are larger than 50 nm; this effect is therefore negligible in the present work. (3) XRD and Raman studies have indicated that the synthesized InN nanostructures are almost strain-free. Moreover, it was also reported that InN has an unusually low pressure coefficient of 0.6–0.9 meV/kbar.² Thus the strain effect cannot be responsible for the larger shift of the band gap. (4) The Burstein-Moss effect is another important factor that affects the optical band gap. It has been reported that the optical absorption edges of InN films shift from 0.7 to 1.7 eV when their free electron concentrations increase from 10^{17} to 10^{20} cm⁻³.^{26,27} Moreover, Chang *et al.* have studied the transport properties of single InN nanowires, and have observed that InN nanowires have metallic conduction and low resistivity of $\sim 4 \times 10^{-4} \ \Omega$ cm with high electron concentration.²⁹ Thus, the Burstein-Moss shift is a very plausible cause for the blueshift of the optical band gap in our case due to the high electron concentrations of the InN nanostructures, as indicated by Raman scattering. However, more work is needed to study the fundamental band gap of InN material.

In conclusion, we have reported a simple, catalyst-free, normal pressure CVD method to prepare InN nanowires and nanotubes. XRD, EDX, SAED, and HRTEM studies show that the synthesized products are of high purity, and have a single crystalline wurtzite structure growing along the *c*-axis direction. Optical transmission measurements determine the optical band gaps to be 1.26 and 1.05 eV for different samples. Burstein-Moss shift is attributed as the factor that affects the energy gap of InN nanostructures.

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- ¹V. Yu. Davydov, A. A. Klochikhin, R. P. Seisyan, V. V. Emtsev, S. V. Ivanov, F. Bechstedt, J. Furthmüller, H. Harima, A. V. Mudryi, J. Aderhold, O. Semchinova, and J. Graul, Phys. Status Solidi B **229**, R1 (2002).
 ²J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, H. Lu, W.
- J. Schaff, Y. Saito, and Y. Nanishi, Appl. Phys. Lett. 80, 3967 (2002).
- ³T. Matsuoka, H. Okamoto, M. Nakao, H. Harima, and E. Kurimoto, Appl. Phys. Lett. **81**, 1246 (2002).
- ⁴J. Goldberger, R. He, Y. Zhang, S. Lee, H. Yan, H. Choi, and P. Yang, Nature (London) **422**, 599 (2003).
- ⁵Q. Wu, Z. Hu, X. Wang, Y. Lu, X. Chen, H. Xu, and Y. Chen, J. Am. Chem. Soc. **125**, 10176 (2003).
- ⁶S. D. Dingman, N. P. Rath, P. D. Markowitz, P. C. Gibbons, and W. E. Buhro, Angew. Chem., Int. Ed. **39**, 1470 (2000).
- ⁷J. Zhang, L. Zhang, X. Peng, and X. Wang, J. Mater. Chem. **12**, 802 (2002).
- ⁸T. Tang, S. Han, W. Jin, X. Liu, C. Li, D. Zhang, C. Zhou, B. Chen, J. Han, and M. Meyyapan, J. Mater. Res. **19**, 423 (2004).
- ⁹C. H. Liang, L. C. Chen, J. S. Hwang, K. H. Chen, Y. T. Hung, and Y. F. Chen, Appl. Phys. Lett. **81**, 22 (2002).
- ¹⁰M. C. Johnson, C. J. Lee, E. D. Bourret-Courchesne, S. L. Konsek, S. Aloni, W. Q. Han, and A. Zettl, Appl. Phys. Lett. **85**, 5670 (2004).
- ¹¹S. Vaddiraju, A. Mohite, A. Chin, M. Meyyappan, G. Sumanasekera, B. W. Alphenaar, and M. K. Sunkara, Nano Lett. 5, 1625 (2005).
- ¹²C. K. Chao, H.-S. Chang, T. M. Hsu, C. N. Hsiao, C. C. Kei, S. Y. Kuo, and J.-I. Chyi, Nanotechnology **17**, 3930 (2006).
- ¹³M. Hu, W. Wang, T. T. Chen, L. Hong, C. Chen, C. Chen, Y. Chen, K. H. Chen, and L. C. Chen, Adv. Funct. Mater. **16**, 537 (2006).
- ¹⁴S. Luo, W. Zhou, W. Wang, Z. Zhang, L. Liu, X. Dou, J. Wang, X. Zhao, D. Liu, Y. Gao, L. Song, Y. Xiang, J. Zhou, and S. Xie, Appl. Phys. Lett. 87, 063109 (2005); Small 1, 1004 (2005).
- ¹⁵B. Schwenzer, L. Loeffler, R. Seshadri, S. Keller, F. F. Lange, S. P. Den-Baars, and U. K. Mishra, J. Mater. Chem. **14**, 637 (2004).
- ¹⁶L. Yin, Y. Bando, D. Golberg, and M. Li, Adv. Mater. (Weinheim, Ger.) 16, 1833 (2004).
- ¹⁷K. Sardar, F. L. Deepak, A. Govindaraj, M. M. Seikh, and C. N. R. Rao, Small 1, 91 (2005).
- ¹⁸M. Yoshimoto, H. Yamamoto, W. Huang, H. Harima, J. Saraie, A. Chayahara, and Y. Horino, Appl. Phys. Lett. **83**, 3480 (2003).
- ¹⁹A. G. Bhuiyan, K. Sugita, K. Kasashima, A. Hashimoto, A. Yamamoto, and V. Yu. Davydov, Appl. Phys. Lett. 83, 4788 (2003).
- ²⁰L. Yin, Y. Bando, J. Zhan, M. Li, and D. Golberg, Adv. Mater. (Weinheim, Ger.) **17**, 1972 (2005).
- ²¹E. P. A. M. Bakkers and M. A. Verheijen, J. Am. Chem. Soc. **125**, 3440 (2003).
- ²²X. Wang, S. Che, Y. Ishitani, and A. Yoshikawa, Appl. Phys. Lett. 89, 171907 (2006).
- ²³V. Yu. Davydov and A. A. Klochikhin, Semiconductors 38, 861 (2004).
- ²⁴A. Kasic, M. Schubert, Y. Saito, Y. Nanishi, and G. Wagner, Phys. Rev. B 65, 115206 (2002).
- ²⁵D. Olego and M. Cardona, Phys. Rev. B **24**, 7217 (1981).
- ²⁶V. M. Naik, R. Naik, D. B. Haddad, J. S. Thakur, G. W. Auner, H. Lu, and W. J. Schaff, Appl. Phys. Lett. **86**, 201913 (2005).
- ²⁷J. Wu, W. Walukiewicz, S. X. Li, R. Armitage, J. C. Ho, E. R. Weber, E. E. Haller, H. Lu, W. J. Schaff, A. Barcz, and R. Jakiela, Appl. Phys. Lett. 84, 2805 (2004).
- ²⁸T. V. Shubina, S. V. Ivanov, V. N. Jmerik, D. D. Solnyshkov, V. A. Vekshin, P. S. Kop'ev, A. Vasson, J. Leymarie, A. Kavokin, H. Amano, K. Shimono, A. Kasic, and B. Monemar, Phys. Rev. Lett. **92**, 117407 (2004).
- ²⁹C. Y. Chang, G. C. Chi, W. M. Wang, L. C. Chen, K. H. Chen, F. Ren, and S. J. Pearton, Appl. Phys. Lett. **87**, 093112 (2005).