Well-Aligned Zn-Doped InN Nanorods Grown by Metal-Organic Chemical Vapor Deposition and the Dopant Distribution

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ABSTRACT: We report the synthesis and characterization of Zn-doped InN nanorods by metal-organic chemical vapor deposition. Electron microscopy images show that the InN nanorods are single-crystalline structures and vertically well-aligned. Energy-dispersive X-ray spectroscopy analyses suggest that Zn ions are distributed nonhomogenously in InN nanorods. Simulations based on diffusion model show that the doping concentration along the radial direction of InN nanorod is bowl-like: from the exterior to the interior, the doping concentration decreases, and such dopant distribution result in a bimodal EDXS spectrum of Zn across the nanorod. The study of the mechanism of doping effect is useful for the design of InN-based nanometer devices. Also, high-quality Zn-doped InN nanorods will be very attractive as building blocks for nano-optoelectronic devices.

Introduction

Recently, indium nitride (InN) has attracted much interest because of its narrow direct band gap and superior transport properties, and it is a promising material for high-efficiency IR emitters, detectors, high-frequency electronic devices, and so on.¹ Thanks to the long and persistent efforts, various InN nanostructures have been acquired.²⁻⁷ Up to now, nanostructure-based InN transistors, sensors, terahertz emitters, and field emitters have been demonstrated, and more novel applications of InN nanostructures are expected to happen.⁸⁻¹¹ After the boom period of InN nanostructures, the burning question now is how to acquire high crystal quality InN nanostructures, which are controllable in doping type and the doping concentration. As long as this question is solved, InN nanostructures will show greater attraction just like other semiconductor nanostructures.^{12–14} However, doping in InN nanostructures was seldom reported. As a p-type dopant in other III nitride semiconductors, zinc has been widely studied,^{15,16} whereas the research on the doping behaviors of zinc during InN growth is still extremely insufficient.¹⁷

On the other hand, there has been great interest in the study of doping in nanostructures.^{18–20} And much research showed the dopant distribution in nanostructures was a crucial problem for the design of nanometer semiconductor devices.¹⁹ There is often a homogeneous distribution in the intentionally doped nanostructures acquired by doping during the growth process.^{18,20} But is this situation always true?

Herein, we report the successful synthesis of vertically wellaligned, Zn-doped InN nanorods by metal-organic chemical vapor deposition (MOCVD). X-ray diffractometry analysis and electron microscopy images indicated that the InN nanorods are single-crystalline structures and have a perfect grown direction along the *c*-axis direction. More intriguing, energy-dispersive X-ray spectrometry (EDXS) analysis revealed that the Zn ions are distributed nonhomogenously in InN nanorods.

Experimental Section

The Zn-doped InN nanorods were synthesized in a homemade MOCVD system, which was demonstrated by previous researchers in our group.²¹ C-plane sapphires were used as substrates. Trimethylindium (TMIn) and ammonia were used as precursors, and diethylzinc (DEZn) was dopant. High-purity nitrogen was used as carrier gas. Before growth, the sapphire wafer was heated under a hydrogen flow at 1050 °C for 20 min to remove the adsorbed water molecules and activate sapphire surface. Subsequently, sapphire wafer was nitridized for 3 min under a mixed gas of H2 and NH3 with a flow rate of 3 SLM (standard liter per minute), respectively. The temperature was then cooled to 550 °C, and InN nanorods were grown at atmospheric pressure. For InN nanorods growth, TMIn (16 µmol/min) and DEZn (0.7 µmol/min) flows were introduced into the MOCVD chamber. The flow rate of N2 and NH₃ is 3 SLM, respectively. The growth time for InN nanorods was 40 min. Before InN nanorod growth, 120 nm GaN buffer layer was deposited. Finally, the TMIn and DEZn currents were cut off and the furnace was cooled to room temperature. Ammonia was maintained during cooling in order to prevent the decomposition of InN.

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The crystal structure and morphologies of products were examined by X-ray diffractometry (XRD: Philips X'Pert Pro diffractometer), fieldemission scanning electron microscopy (FE-SEM: Hitachi S-4800). The products were dispersed onto copper grids possessing an amorphous carbon film and further characterized with a high-resolution transmission electron microscope (HR-TEM: FEI TECNAI F30, 300 kV and JEM 2010, 200 kV, only for Figure S1 in the Supporting Information) attached to an energy-dispersive X-ray spectrometer.

Nanorod Growth Results

The as-synthesized Zn-doped InN wafer lost the mirrorlike black surface morphology and became blurring and gray. Figure 1 shows the XRD spectra of the InN nanorods. For InN, only diffraction from (002) and (004) planes is observed at 31.45 and 65.52° , respectively. These diffraction patterns agree well with InN of the hexagonal wurtzite structure, which is in agreement with the data on the Joint Committee of Powder Diffraction Standards (JCPDS) card 79–2498 (InN). The diffraction peaks in the spectrum of as-synthesized product at 32.98 and 69.1° correspond to In(101) and In(202) planes (JCPDS: 85-1409), respectively. After the product was dipped in dilute hydrochloric acid (HCl) for 5 min, the diffraction peaks associated with metal indium almost vanished, whereas other diffraction peaks were unchanged.

Typical FE-SEM images of InN nanorods are shown in Figure 2. The nanorods are 200–300 nm in diameter and 2–5 μ m in length, and they are vertically well-aligned. Except some short nanorods with sharp tips, there is a droplet on each InN nanorod

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Figure 1. HR-XRD patterns of InN nanorods. The upper line (black) is the spectrum of as-synthesized sample, and the bottom line (red) is the spectrum of sample after dipping in HCl. The spectrum of as-synthesized is shifted upward along the vertical axis to simplify comparison.



Figure 2. (a) Bird-view SEM image. (b) Tilted-view SEM image. (c, d) Side-view SEM images of as-synthesized and HCl-dipped InN nanorods.



Figure 3. (a) TEM image of two as-synthesized InN nanorods. (b) HR-TEM image of the InN nanorod. Inset: ED pattern taken along the [110] zone axis. (c) EDXS spectrum taken at spot P which is marked in (a). Inset: the composition of the nanorod determined by XEDS.

in Figure 2c. This is strong evidence that the nanorods are grown via the vapor-liquid-solid (VLS) process. Figure 2d shows a cross-sectional image of InN nanorods that were dipped in HCl. Compared with Figure 2c, the droplets on InN nanorods disappeared and quite flat upper surfaces of the nanorods were exposed. HR-XRD analyses showed that there was metal indium phase in the as-synthesized product, and it disappeared after being dipped in HCl. It is reasonable to infer that these droplets on the nanorods are metal indium droplets.

Figure 3a illustrates a typical TEM image of two assynthesized InN nanorods. The nanorod on the right holds a metal droplet and both of them have smooth and abrupt side walls. Figure 3b is the high-resolution lattice image. The interplanar distances of 0.31 nm, 0.28 and 0.27 nm match with the d_{100} , d_{002} , and d_{101} spacing of wurtzite-type InN, respectively. These lattice parameters also indicate that the InN nanorods grow along the *c*-axis. The corresponding electron diffraction (ED) pattern is shown in the inset of Figure 3b, which was taken along the [110] zone axis of the nanorod. It shows that the InN nanorods are single-crystalline.

Energy-dispersive X-ray spectroscopy (EDXS) measurements were carried out to determine the dopant distribution in InN nanorods. To eliminate the possible contamination, samples for EDXS were dipped in HCl for enough time and rinsed in deionized water (DIW). An EDXS spot scan spectrum of marked position in Figure 3a is shown in Figure 3c. Cu signals are generated from copper grids that support the nanorods. The corresponding chemical composition is shown in the inset of Figure 3c, which indicates the InN nanorod is Zn-doped.

Figure 4a shows the EDXS line scan profiles recorded along the axial direction (the red line indicates the scanpath). To our astonishment, the intensity of Zn signal decreases from bottom to top along the axial direction of InN nanorod. It is rather different from the line scan profile of In, which is distributed homogenously in the nanorod. What's more, EDXS line scan profiles across the nanorod (Figure 4b) also show the difference between the distributions of In and Zn. The intensity of In signal



Figure 4. EDXS line scan profiles of In (asterisk) and Zn (dot) (a) along the axial direction and (b) across the InN nanorod. For clarity, Zn profiles are multiplied by 10 and 5, respectively.



Figure 5. (a) Schematic illustration of diffusion model. (b) Simulated dopant intensity profile across the nanorod on the basis of the diffusion model. (c) Simulated dopant intensity profile across the nanorod if the dopant is homogeneously distributed.

at the middle of InN nanorod is higher than that at both sides. It is unimodal and similar to those of Cd and S in Mn-doped CdS which are host elements in CdS.¹⁸ On the contrary, the line scan profile of Zn is bimodal.

Diffusion Model and Discussion

The blue line in Figure 4a is a linear fitting of Zn intensity profile. According to the growth conditions, we attribute the abnormal distribution of Zn to the diffusion behavior of Zn after InN nanorods growth. Figure 5a demonstrates the schematic illustration of the diffusion model discussed here. Once the InN nanorods were grown, they were exposed to the growth ambience containing dopant which could diffuse into InN nanorods from their side walls. The bottoms of the nanorods exposed to the growth ambience longer than the tops, and therefore, the diffusion time decrease proportionately from the bottom to the top along the axial direction. Correspondingly,



Figure 6. The peak position of Zn signal in line scan profile across InN nanorod as a function of diffusion coefficient of Zn in InN. The diffusion time is 20 min and the surface concentration of Zn is 2.0×10^{21} cm⁻³. The red dash dot lines indicate the variation range of the peak position of Zn signal in Figure 4b, and 0 nm at the vertical coordinates indicates the core of the nanorod.

EDXS line scan signal of Zn should become weaker, which was clearly shown in Figure 4a.

To prove this assumption, we simulate the dopant distribution across the nanorod basing on the diffusion model. It should mention that almost no Zn was detected in the metal In droplets on the top of InN nanorods (within the detection limit, see Figure S1 in the Supporting Information). Considering our growth conditions (a flow rate of 3 SLM for N₂, 3 SLM for NH₃, 0.2 SLM for N₂ used as carrier gas, 16 µmol/min for TMIn, and 0.7 µmol/min for DEZn; 550 °C at atmospheric pressure), according to Dalton's law of partial pressures, the vapor pressure of TMIn and DEZn in the growth ambience was about 5.86 and 0.26 Pa, respectively. The melting point of indium and zinc is 156.6 and 419.6 °C, and the saturated vapor pressure of liquid indium and zinc is 2.4×10^{-5} Pa and 557.2 Pa at 550 °C, respectively.²² Such a low vapor pressure of zinc in the growth ambience led to a very low Zn composition ($\sim 0.01\%$, atomic percent) in the metal droplet on the top of InN nanorod. This was proved by Figure S1 in the Supporting Information, combining with XRD and SEM results. So, we could neglect the Zn doping from the catalyst heads.

The scan line in Figure 4b (marked by a short red line) is about located at the middle of the nanorod; therefore, the diffusion time for InN here is about 20 min. To determine the surface concentration of Zn in InN nanorod, we also measured EDXS line scan profiles across the nanorod at the bottom and at the place near the top were also measured (see Figure S2 in the Supporting Information). It is found that the mol ratio of indium to zinc is about 13.5 at the initial 2 or 3 test points at the edge of nanorod where the doping concentration is very close to the surface concentration of Zn in InN nanorod. So the surface concentration of Zn is about 2.0×10^{21} cm⁻³. Also, the diffusion coefficient of Zn in InN at 550 °C is unknown for us because of the lack of previous research on the doping behaviors of zinc during InN growth;¹⁷ however, the peak position of Zn signal (Figure 4b) in the line scan profile across the nanorod depends on the diffusion coefficient of Zn in InN. This relation is shown in Figure 6. The larger the diffusion coefficient of Zn, the interior the peak position. According to the peak position of Zn signal in Figure 4b, the diffusion coefficient of Zn in InN at 550 °C is estimated to be 2.0×10^{-14} cm²/s.

Because of the existence of the metal In droplets on the top of InN nanorods, Zn is considered to diffusion into InN nanorod from the side wall. Following assumptions are suggested to simplify the modeling and calculations: (a) quantum size effect is negligible, i.e., the diffusion behavior of Zn in InN nanorods obeys to Fick's diffusion law; (b) the diffusivity of Zn in InN is constant, extrinsic diffusion effect is neglected; (c) InN nanorod owns an invariable growth rate during the whole growth stage. In our experiment, DEZn was supplied along with TMIn stably. The supply of Zn atoms at the nanorods surfaces was invariable until the growth stage was terminated.

Figures S3-S5 in the Supporting Information show the timedependent dopant distributions profile along the radial direction at a fixed location. As seen in Figures S3-S5 in the Supporting Information, the dopant is mostly in the outer shell of InN nanorod at the initial stage (Figure S3 in the Supporting Information) and then diffuses into the core gradually; the dopant distribution profile along the radial direction is bowl-like and the doping concentration at the center in Figure S5 in the Supporting Information is higher than that in Figure S4 in the Supporting Information. The simulated dopant distribution profile on the cross section is shown in Figure 5b. There are two maxima signal at the edge of InN nanorod. This just proves that the bimodal profile of Zn in EDXS is caused by the diffusion behavior of Zn in InN nanorod. In Radovanovic's work, bimodal dopant intensity profile only exist when assume that all of the dopant is localized in the shell.¹⁸ We provide experimental evidence for nonhomogeneous dopant distribution in nanostructures here. Also, we note simulated Zn intensity profile here has a weaker dip at the center of nanorod comparing with the model calculation of the Mn EDX profile in Radovanovic's work. This is the result that the Zn ions can diffuse into the core of InN nanorods in our model as shown in Figures S3-S5 in the Supporting Information; hence the intensity of Zn signal at the center of nanorod is enhanced.

For comparison, Figure 5c is the intensity profile if the dopant is distributed homogenously in the InN nanorod. It shows that the homogenously distributed dopant in the nanorod causes only one peak when the EDXS e-beam scans across the nanorod and the peak locates at the center of the nanorod. As the host element in InN nanorod, the intensity profile of In in Figure 4b has a similar line shape and proves our simulation.

Unlike Si, GaAs, or ZnO, which are robust enough to endure annealing, InN is tender at high temperature. Therefore, doping during the growth process is good enough for InN. The study of the mechanism of doping effect will be helpful for controlled doping in InN-based nanometer devices.

Conclusion

In summary, the vertically well-aligned Zn-doped InN nanorods have been synthesized on C-plane sapphires by MOCVD successfully. XRD, SEM, and TEM measurements show that these InN nanorods have good single-crystalline quality, and they grow along the *c*-axis direction; they have abrupt side walls and most of them hold metal In droplets on the top. EDXS spectra reveal that InN nanorods are Zn-doped and the dopant distribution in InN nanorods is nonhomogeneous. The simulations based on a diffusion model show that the spectrum of EDXS across the nanorod will be bimodal if the dopant diffuse into InN nanorods from their side-walls, whereas homogeneous dopant distribution in InN nanorod just causes a unimodal line shape. These results are in accord with the EDXS line scan spectra of Zn and In when an e-beam is scanned across the nanorod and give credible evidence for our assumption based on diffusion behavior of Zn in InN. These high-quality Zn-doped InN nanorods with abrupt side walls and flat upper surfaces provide opportunities for fundamental research and will be very attractive as building blocks for nano-optoelectronic devices.

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Supporting Information Available: Simulations of time-dependent dopant distributions across the nanorod (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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