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Synthesis of [100] Wurtzite InN Nanowires and [011] Zinc-Blende InN Nanorods *

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One-dimensional wurtzite InN nanowires and zincblende InN nanorods are prepared by chemical vapour deposition (CVD) method on natural cleavage plane (110) of GaAs. The growth direction of InN nanowires is [100], with wurtzite structure. The stable crystal structure of InN is wurtzite (w-InN), zincblende structure (z-InN) is only reported for 2D InN crystals before. However, in this work, the zincblende InN nanorods [011] are synthesized and characterized. The SEM and TEM images show that every nanorod shapes a conical tip, which can be explained by the anisotropy of growth process and the theory of Ehrlich–Schwoebel barrier.

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Group Ⅲ-nitride semiconductor materials have attracted much attention in the last few decades because of their potential in electronic and optoelectronic applications.[1] Among them, indium nitride (InN) is a promising but challenging semiconductor material, which has the smallest effective electron mass and direct bandgap (0.6–0.7 eV),[2−4] the highest mobility and saturation velocity, and the largest drift velocity at room temperature compared with all other Ⅲ-nitrides. The novel properties make InN a candidate material for photonic devices such as photodetectors, high efficiency solar cells, LEDs in the infrared light region, and so on.[5]

The one-dimensional (1D) nanostructure is an ideal system for investigating the dependence of electrical transport, optical and mechanical properties on size and dimensionality. It is expected to play an important role as both interconnects and functional components in the fabrication of nanoscale microelectronic and optoelectronic devices.[6] 9The low dissociation temperature[7] and lack of lattice matched substrate have hampered synthesis of high-quality 1D InN nanostructures. Therefore, there are only few reports about 1D InN nanostructures, compared with 2D structures of InN and 1D GaN nanostructures.

The growth direction of InN nanowires is variable, and most of the existing reports about the synthesis of InN nanowires show a growth direction along [110]. In this work, the growth direction of InN nanowires is along [100], which corresponds to Ref. [8]. Furthermore, the stable crystal structure of InN is wurtzite (w-InN), zincblende structure (z-InN) has only been reported for 2D InN crystals. In this experiment, wurtzite InN nanowires and zincblende nanorods have been synthesized on the natural cleavage plane of GaAs [i.e. the (110) plane].

The synthesized products were characterized by XRD, SEM., TEM, HR-TEM, SAED and EDX.

The InN nanorods and nanowires were synthesized by chemical vapour deposition (CVD) method on cleavage plane of GaAs [i.e. (110) plane] substrates in a horizontal high-temperature resistance furnace. The main reaction is

$$2\,\mathrm{In}\,(s) + 2\,\mathrm{NH_3}\,(\mathrm{g}) = 2\,\mathrm{InN}\,(s) + 3\,\mathrm{H_2}\,(\mathrm{g}).$$

The chemical reaction process of Indium and ammonia was carried out at 900°C. GaAs(001) substrates with natural cleavage plane (110) were located in the downstream zone with 550°C growth temperature. The whole growth process was continued for one hour under the standard atmosphere and without any catalyst. The percentage purity and flow rate of ammonia is 99.999% and 0.2 L/min, respectively.

The formation of the nanowires and nanorods can be divided into three steps. In the first step, indium chunk was evaporated and the ammonia was decomposed in the 900°C zone. In the second step, indium vapour reacted with the decomposed ammonia, at the same time being driven by the flowing ammonia atmosphere. Finally, the mixed reactant deposited on GaAs substrates in 550°C zone, and these nuclei further grew into nanowires and nanorods with the incoming mixed reactant.

The crystal structures of the synthesized products were investigated using x-ray powder diffraction (XRD). The morphologies and size distribution of the as-prepared nanowires and nanorods were characterized using scanning electron microscope (SEM) and

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transmission electron microscope (TEM). The composition of InN nanowires and nanorods has been determined using energy dispersive x-ray spectrometry (EDX), which is equipped on SEM. In addition, the crystal structures and morphologies were also studied by high-resolution TEM (HRTEM) equipped with selected area electron diffraction (SAED).

XRD techniques are used to study the crystal structure and the composition of products. The XRD spectrum of InN samples is shown in Fig. 1. Two different phases of hexagonal InN (h-InN) and cubic InN (c-InN) can be indexed. The c-InN peaks at 31.0° (111) and 35.9° (200) indicate a lattice constant of $\alpha_c = 4.99\,\text{Å}$ which is close to previous values.[9,10] The h-InN(110) and h-InN(103) show that the hexagonal InN has a lattice parameter of $\alpha_h = 3.535\,\text{Å}$ and $c_h = 5.705\,\text{Å}$.

The morphology of the synthesized products is examined by SEM (JEOL JSM-7000F). A typical SEM image of InN nanowires and nanorods is shown in Fig. 2(a). The SEM image demonstrates that InN nanowires and nanorods can be obtained under standard atmosphere without any catalyst. These nanowires growing out of the cleavage surface appear to be uniform both in diameters and lengths. Detailed TEM and SEM observations indicate that the diameters are around 50 nm while the lengths are 10–15 μm, with aspect ratios exceeding 200:1. Typical SEM image of single nanowire is shown in Fig. 2(b), which displays a very uniform diameter. Contrarily, the size of different nanorod is less-regular, and the diameter gradually decreases from bottom to top in single nanorod and shapes a conical tip (Fig. 2(c)).

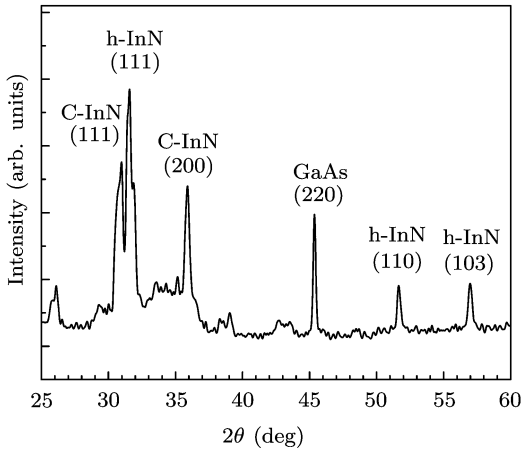


Fig. 1. Typical XRD spectrum of products.

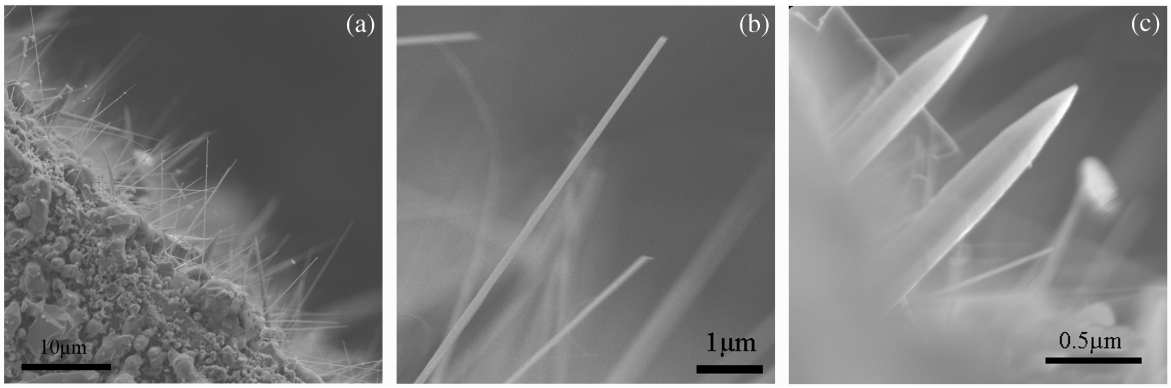


Fig. 2. (a) SEM image of nanowires and nanorods, (b) typical SEM image of nanowires, (c) typical SEM image of nanorods.

An EDX (Oxford 350) equipped on SEM is engaged to determine the composition of single nanowire. The EDX analysis indicates that the nanowires consist of indium and nitrogen elements (with the atomic ratio of In and N being about 1:1, compared to that of the InN phase). To better observe the morphology and examine the crystal structures of individual InN nanowire, the TEM and SAED are used. Figure 3(a) is a typical bright-field TEM image of a single InN nanowire. The nanowire looks rather homogeneous, suggesting its good crystalline structure. SAED pattern recorded perpendicular to long axis of the nanowire is shown in Fig. 3(b). It shows that the growth direction of these InN nanowires is parallel to the [100] direction. Similar results have been acquired in other nanowires, as well as different positions in a single nanowire. Further insight into the structure of as-grown InN nanowire is provided by the HRTEM (JEM-4000EX) (Fig. 3(c)). The distance of adjacent lattice planes is about 0.30 nm which is exactly consistent with the planar spacing between two (100) crystal planes. This confirms the conclusion by the SAED pattern that the growth direction is along [100] again. It is worth mentioning that most of the existing reports about the synthesis of InN nanowires show a growth direction along [110], and [110] growth direction has the lowest free energy.[11,12] In this work, however, the growth direction of InN nanowires is along [100], which corresponds with Ref. [8]. The (100) plane in the SAED patterns

and the HRTEM image can be indexed to hexagonal InN.

The TEM, EDX, SAED and HR-TEM are also used to characterize the InN nanorods in detail. The EDX results confirm that the nanorods are composed of indium and nitrogen element (with the atomic ratio of 1:1). A typical bright-field TEM image is depicted in Fig. 4(a), revealing the smooth surface of InN nanorods. Figure 4(b) shows the typical SAED pattern of an individual nanorod. The SAED pattern with Bragg spots corresponding to (022), (333), and (100) planes can be indexed as a single-crystal zincblende structure with the growth direction along [011]. HRTEM image (Fig. 4(c)) of the individual nanorod gives interplanar spacings of 0.50 nm and 0.35 nm, which exactly correspond to (100) and (022) plane of zincblende InN, respectively. This image also convincingly proves the single-crystalline character feature of nanorod with its growth direction parallel to [011], which are in agreement with the SAED results. It is noteworthy that zincblende InN[13] has only been reported for 2D crystals, never for 1D nanostructures.[9] In Ref. [9], the authors have reported the growth of InN nanorods exhibiting a mixture of wurtzite and zincblende phases. In this work, however, the InN nanorods are successfully synthesized with single zincblende phase.

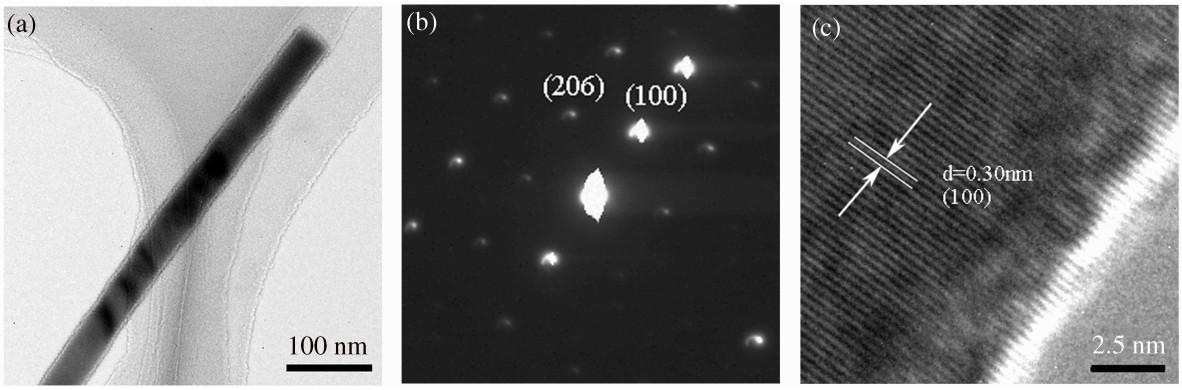


Fig. 3. (a) Bright-field TEM image of a single InN nanowire, (b) SAED pattern of single nanowire, (c) HRTEM image of single nanowire.

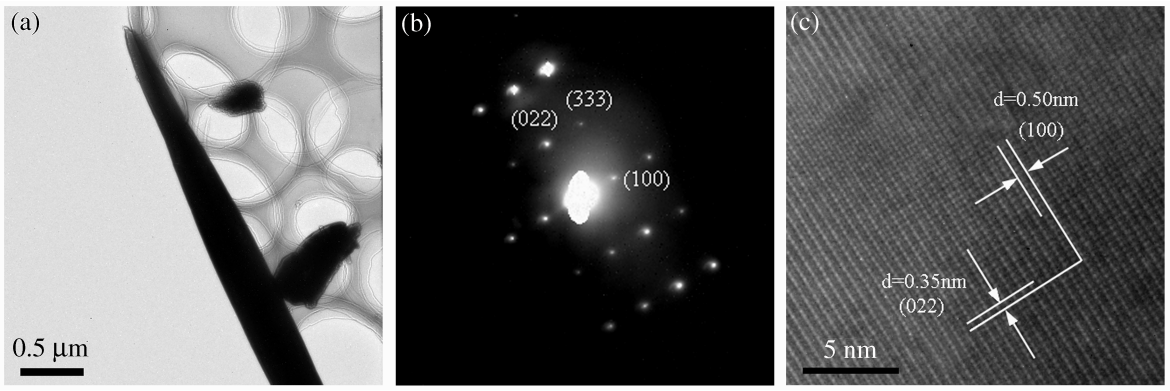


Fig. 4. (a) Bright-field TEM image of a single InN nanorod, (b) SAED pattern of single nanorod, (c) HRTEM image of single nanorod.

In the experiments, the 1D nanostructures are synthesized only on natural cleavage plane of GaAs (i.e. (110) plane), and the same nanostructures have not been found on the surface of (001). It is because the surface energies of (001) plane and (110) plane are different.[14] The experiments show that the crystallographic plane of GaAs (110) is more suitable for the growth of 1D InN nanostructures.

As mentioned before, the InN nanorods grow along [011], and each nanorod shapes a conical tip. This shape can be explained by anisotropy of growth process and the theory of Ehrlich–Schwoebel barrier. The anisotropic properties cause the variational growth rates along different growth directions. For InN nanorods, the growth rate of crystal plane (011) is the fastest. However, the lower rate growth also occurs on other directions which are perpendicular to [011]. In nanorods, the growth time of bottom is longer than that of the top, and that causes the decreasing diameters on the nanorod. The Ehrlich–Schwoebel barrier

is ubiquitous in the growth process of crystallography materials.[15,16] When atoms diffuse between the adjacent lattice planes, they must overcome the E-S barrier.[17] The atoms which preferentially deposit on the end of the rod are difficult to transfer to the under crystal planes, so as the growth process continues, the plane of the end decreases gradually. Finally, the plane disappears and the whole rod shapes a conical tip.[18]

In summary, InN nanowires and nanorods have been synthesized on the natural cleavage plane of GaAs by CVD method. The SEM and TEM images show that the nanowires are uniform with diameters around 50 nm and lengths of 10–15 μm, while the size of nanorods is less-regular and has the shape of a conical tip. The SAED patterns and HRTEM images confirm that the nanowires belong to wurtzite structures and grow along the [100] direction, while the nanorods belong to zincblende structures and grow along the [011] direction.

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