[0001]-Oriented InN Nanoleaves and Nanowires: Synthesis, Growth Mechanism and Optical Properties

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Abstract Novel indium nitride (InN) leaf-like nanosheets and nanowires have been grown on Si substrate by chemical vapor deposition method. The characterization results indicate that the samples are single-crystalline, and the growth direction of the nanowires and nanoleaves is [0001]. The growth mechanism of the InN nanoleaves is following the pattern of vapor–liquid–solid process with a three-step growth process. In addition, the room temperature photoluminescence spectra of two nanostructures show band-to-band emissions around 0.706 eV, where the emission from single nanoleaf is stronger than nanowire, showing potential for applications in optoelectronic devices.

KEY WORDS: Novel indium nitride (InN); Chemical vapor deposition (CVD); Nanoleaf; Crystal structure; Photoluminescence (PL)

1 Introduction

As representative group III–V nitride semiconductors [1], InN materials are important for their interesting properties, such as high electrical conductivity and electron mobility [2]. In addition to thin film-type InN materials, the research on InN nanostructures has attracted much attention for their potential for advanced applications in the nanoscale devices with feasible tunability of properties, applied in high-speed field effect transistors (FETs) [3], biosensors [4],

electrochemical sensor [5], high-output piezoelectric nanogenerators [6] and terahertz spectroscopy [7].

The properties of nanostructures usually depend on its size and shape. Various InN nanostructures, including one-dimensional (1D) nanotubes, two-dimensional (2D) nanosheets and three-dimensional (3D) nanoflowers, have been synthesized by different physical and chemical methods [8–15]. Reports on the ascendant InN epitaxial nanocolumns [15] were synthesized by controlling two factors of various substrate temperatures and III/V ratios, indicating the further development of the 2D InN nanostructures. For 2D nanomaterials, those with leaf-like morphology represent a special group of nanostructures, like GaN and ZnO hexagonal nanoplates, with potential in optical application [16–21]. For instance, symmetric nanoplates are excellent source for whispering gallery mode nanolaser resonators [22, 23], and nanodisks or nanobelts are widely used as gas sensors and photodetectors [24, 25]. Nevertheless, studies of the 2D structure of InN nanomaterials are scarce so far. Previously we have demonstrated on the growth and characterization of two kinds of InN nanomaterials (nanowires and nanonecklaces) by a simple catalytic vapor deposition technique [26].

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Here in this present study, we have synthesized InN leaf-like nanosheets and nanowires via the cost-effective, clean and rapid CVD method [26]. The morphology, composition and microstructure of the products were systematically characterized. The growth mechanism of InN nanoleaves materials was analyzed and discussed in detail. The three-step growth mechanism was presented based on temperature-dependent growth observation. Furthermore, room temperature photoluminescence (PL) spectra of two InN nanostructures demonstrated fairly good optical properties.

2 Experimental

The single-crystal InN nanoleaves reported here were grown by CVD method in the presence of gold colloid (BBI solution, thickness: 60 nm) as the catalyst. The raw materials were pure In powder (99.999%, Xiya reagent) and NH_3 gas (99.99% purity, Messer). The p-type silicon (100) substrate coated with gold colloid was placed face-down above the indium powders loaded in the quartz boat, and the whole facilities were placed at the central heating zone of tubular resistance furnace. Before heating, the quartz tube was pumped to around 3 Pa and flushed several times with Ar (carrier gas: 99.999% purity) to remove impurities. Then, the center of the furnace was heated up to the reaction temperature of 700 °C with Ar and kept at this temperature for 100 min under NH_3 with a flow rate of 150 sccm. Finally, the furnace was naturally cooled down to room temperature with Ar, and gray and black-colored products were formed on the silicon substrate.

The morphological and microstructural properties of the as-synthesized products were characterized by field emission scan electron microscopy (SEM; Model UItra 55) equipped with energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) on a Philips X' Pert PRO diffractometer equipped with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418$ nm), transmission electron microscopy (TEM; Model Libra 200 PE, operated at 200 kV), and room temperature PL spectrum (model; in Via) carried out on a Raman microscope using a 514 nm He–Cd laser as the excitation source.

3 Results and Discussion

Figure 1a, b shows the typical SEM images of InN nanostructures in low and high magnification, respectively. It can be clearly seen that the samples are mainly composed of two kinds of InN nanostructures: nanowires and nanoleaves. The typical length and diameter of the individual nanowires range from 3 to 10 μm and 80 to 150 nm.

Highly magnified side-view SEM image of a single nanoleaf reveals that the nanoleaves are with a lateral size of $(15 \pm 0.5) \mu\text{m}$ and a thickness of 100 nm, showing a novel corn leaf-like structure (Fig. 1c). Undoubtedly, the nanoleaves are of thin thickness and flat surface, which has not been reported before. In addition, the co-existence of different morphology nanomaterials indicates that the CVD growth of various nanostructures may have a large interval range in growth process. The vapor–liquid–solid (VLS) growth mechanism [27] is promoted by the existence of gold nanoparticles; Au acts as a catalyst in order to reduce the activation energy for develop nucleation position greatly.

Figure 2 displays in more detail typical XRD patterns of InN nanostructures. All of the strong diffraction peaks in the spectrum can be indexed to hexagonal wurtzite structure InN (JCPDS card No. 50-1239, $a = 0.353$ nm, and $c = 0.57$ nm). It is in good agreement with the previously reported values of InN bulk crystals [28]. The full-width at half-maximum (FWHM) of those peaks is keen-edged, indicating large-sized single crystal. There are some characteristic peaks of other phases (Si, Au, oxides) detected in XRD. The O-related peaks originated from the native oxidation of substrate or the formation of indium oxides potentially. To clearly identify the appearance of oxide peaks, we conclude that the diffraction peaks about oxides slightly match with the reported In_2O_3 nanostructure [29] (JCPDS card No. 06-0416) with cubic system. Simultaneously, we can see the (100) diffraction peak appeared which belongs to InN nanostructure, and the (002) diffraction peak at 31.330° and the (101) diffraction peak at 33.156° are closer to InN but In_2O_3 , where the two peaks' relative intensities are in accordance with InN crystal with hexagonal wurtzite structure. Therefore, the related O peaks might be the introduced impurities and the native SiO_2 formed on Si substrate.

The EDS measurements were carried out to analyze the chemical composition of the samples. Figure 3a illustrates a representative SEM image of the part of the sample that contains nanowires and nanoleaves, while the EDS spectrum of the marked position in Fig. 3a is shown in Fig. 3b. The EDS spectrum contains six elements: C, N, O, In, Si and Au, and the atomic ratio of In:N is close to 1:1, suggesting a good stoichiometry of the materials. While the silicon peak originates from the substrate, carbon and oxygen peaks are derived from the introduction of the gas outside or oxidation on the substrate [17].

Figure 4a–d clearly shows the TEM images of individual InN nanowire and nanoleaf. Figure 4a shows a typical TEM image of single nanowire with a smooth morphology. A high-resolution TEM (HRTEM) image (Fig. 4b) reveals that the length growth direction of InN nanowire is [0001] with the lattice spacing of 0.281 nm, which is in good

Fig. 1 a, b Less and highly magnified SEM images of the nanoleaf and nanowire structures; c side-view of highly magnified SEM image

Fig. 2 XRD pattern of the InN nanostructure

agreement with the (100) planes of InN hexagonal structure correspondingly [30, 31]. The inset in Fig. 4b is the selected area electron diffraction (SAED) pattern from the corresponding area of nanowire, confirming that the product is single-crystalline and grows directly along the [0001] direction. Figure 4c presents the TEM image of InN nanoleaf showing clearly the round head at the tip of the nanoleaf. Figure 4d shows a lattice-resolved TEM image taken from the edge region of the nanoleaf, and the measured interplanar spacing of the crystalline phase is 0.284 nm, which corresponds to the (101) plane of the hexagonal InN. Synchronously, the illustration of the Fig. 4d shows the HRTEM pattern of the edge region of the nanoleaf. It exhibits a spot pattern of a single-crystal hexagonal phase, no grain boundary was found in the sample, and the length direction of InN nanoleaf is [0001]. Both the HRTEM and fast Fourier transformed (FFT) results demonstrate that the nanoleaves are single crystals with a hexagonal structure. For the purpose of studying the native structure, the atomic accumulation structure model of InN nanoleaves is described in Fig. 4e, f. As is shown in Fig. 4f, the growth direction of nanoleaves is [0001], with the two polar side surfaces being $\{10\bar{1}1\}$ and $\{10\bar{1}\bar{1}\}$. By using the standard lattice parameters of w-InN, the angle

between two corresponding facets on the adjacent facets of leaf-like structure is calculated to be 116° [26], which is closed to the actual measurement of 117.7° (Fig. 4c).

Based on the above results, the leaf-like InN nanostructure exhibits VLS growth mechanism, which is different from the products prepared by solvent method. So far, most of researches about nanomaterials with the growth mechanism of VLS pay attentions to the one-dimensional nanomaterials [32], such as nanowires and nanorods. These nanomaterials show two typical characteristics: (1) the liquid metal catalyst act as the nucleation point of the absorption gas reaction and (2) the metal catalyst particles can be observed at the top of the nanomaterial. As shown in Fig. 5a, b, the metal particles are at the end of nanoleaf and nanowire, which indicates the presence of Au particles. Besides, Au particles are easy to combine with In droplets. Consequently, the size of Au particles has influence on the size of nucleation sites and the surface area of the gas absorption. Therefore, the gold catalyst plays a key role in the growth of the leaf-like nanostructure.

A series of experiments were carried out to study the growth process in detail, and we have recorded the morphology of InN nanostructures at different growth temperatures. As shown in Fig. 6a–d, during the whole growth process of the InN nanostructures, we can conclude that the size of the nanoleaf increase as the temperature increases continuously from 500 to 650 °C. There are obviously three steps to the growth process of InN nanostructures as shown in Fig. 6e. The first step is the formation of nucleation particles. Indium atoms and ammonia molecules reacted and nucleate with the assistance with gold catalyst and nanowire-like structures start to grow (Fig. 6a). The next step is the growth of nanowires. The arrival of new In and N atoms can be repeated to form new InN layer in the growth direction, which is explained schematically in Fig. 6b, and it is quite clear that the InN nanowire is followed by the VLS growth mechanism [33]. The last step is the formation of leaf-like InN morphology. This process is embodied through Fig. 6c, d. Based on all above-related process, the growth procedure can be concluded by Fig. 6e. In order to understand the mechanism of InN nanoleaf

Fig. 3 SEM image of the as-grown InN nanoleaves **a** and EDS spectrum corresponding to the spot marked spectrum 37 **b**

Fig. 4 **a** TEM image of the individual nanowire, **b** corresponding HRTEM image and SAED pattern (the inset) of the nanowire, **c** TEM image of the individual nanoleaf, **d** corresponding HRTEM image and FFT pattern (the inset) of the nanoleaf, **e** model of InN atomic accumulation structure, **f** crystal structure of InN nanoleaf, showing the positively or negatively charged $\{10\bar{1}1\}$ and $\{10\bar{1}\bar{1}\}$ planes

deeply, the size of (0001) surface was gradually decreased and the side facets of $\{10\bar{1}1\}$ and $\{10\bar{1}\bar{1}\}$ planes appeared to form the leaf-like structure. Because the terminated In^{3+} - $\{10\bar{1}\bar{1}\}$ and N^{3-} - $\{10\bar{1}1\}$ planes had possessed finite charges and dipole moments [26], they would result in the positive and negative electrostatic surface energy increase. To keep the structure stable, the total surface free energy including the surface energy and the electrostatic surface energy should be minimized, when the $\{10\bar{1}1\}$ and $\{10\bar{1}\bar{1}\}$ planes continue to crystallize with increasing electrostatic surface energy, but the $\{10\bar{1}1\}$ and $\{10\bar{1}\bar{1}\}$ side facets have

opposite termination to keep the conservation of energy. The alternation of the dipole moments and the change of the electrostatic surface energy will lead to repeated formation of In^{3+} - $\{10\bar{1}\bar{1}\}$ and N^{3-} - $\{10\bar{1}1\}$ side facets along the *c*-axis direction and finally produce the InN nanoleaf. Simultaneously, it also can be concluded that the longitudinal growth influences the lateral growth process. An axial perturbation due to fluctuation of growth conditions may cause the bulging of middle region of the structures and result in a leaf-like InN morphology. In the whole growth process, literature data of the Gibb's free energy for the

Fig. 5 SEM images of InN nanowires **a** and InN nanoleaf **b** based on growth mechanism

Fig. 6 Whole growth process of InN nanowires and nanoleaves at different growth temperatures keeping in accordance with the same growth conditions: **a** 500 °C, **b** 550 °C, **c** 600 °C, **d** 650 °C, **e** schematic diagram of InN nanostructure growth in Si (P type: 100) substrate

formulation of InN, under conditions close to ours, is listed as follows [34]:

Figure 7a shows the room temperature PL spectrum of the nanowire and nanoleaf. The PL peak emission is located at around 0.706 eV which is attributed to Mahan excitonic recombination [35]. The band-to-band Mahan emission transition was in agreement with that of the high-quality nanorods and epitaxial films, which is also consistent with that measured in n-type degenerate InN [36]. In addition, the FWHM of the band-to-band emission peak of the single nanowire and nanoleaf are 26.14 and 25.17 meV, respectively, indicating that these two nanostructures have high crystalline quality. Otherwise, the FWHM of nanoleaf is lower than that of nanowire,

showing a higher degree of crystallinity. Notably, the emission intensity from the nanoleaf is stronger due to the fact that the nanoleaf is with good crystallinity [37] and generates the effect of multi-scattering inside itself with the average crystalline size of leaf-like structure greatly larger than nanowire, thus resulting in the high recombination probability at band edge region being improved. In addition, the temperature-dependent PL spectra of InN nanoleaf are shown in Fig. 7b, indicating a weak shift (peak position) from 0.706 eV at 180 K to 0.698 eV at 300 K. Simultaneously, a shoulder is weakly visible at ~64 meV below the main transition due to the coupling of longitudinal (LO) phonons [35]. The thermal variation of the band gap energy can be calculated to be 8 meV as a result of the lattice expansion and electron–phonon interaction [38] and broadens with increasing

Fig. 7 **a** PL spectra of nanoleaf and nanowire at room temperature (300 K), **b** temperature-dependent PL spectra of nanoleaf

temperature. This line-shape analysis confirms that the emission of nanoleaf is mainly due to the Mahan excitation. Consequently, these high-quality InN crystallites have potential applications in optoelectronics, and may be widely used in IR nanocavity lasing.

4 Conclusion

Two different kinds of InN nanostructures including nanoleaves and nanowires were synthesized by CVD. The synthesis of high-purity single-crystalline InN nanostructures with hexagonal wurtzite crystalline was obtained. The nanowire and nanoleaf growth were preferentially along [0001] direction. The nanowire and leaf-like structures grew along its axial direction via the VLS mechanism. The room temperature PL spectra of these InN nanostructures demonstrated the emission peak around 0.706 eV. These results demonstrate that leaf-like InN nanosheets are promising for near-infrared optoelectronics applications.

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