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Chemical vapor deposition growth of InN nanostructures: Morphology regulation and field emission properties

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ABSTRACT

The facile synthesis of InN nanostructures is of great importance due to their wide potential applications in (opto)electronic devices. Herein we reported the synthesis of InN nanostructures through a convenient chloride-sourced chemical vapor deposition method with simple processing and free of catalyst. The morphologies of the InN products were regulated from one-dimensional nanocones and hexagonal nanoprisms to octahedrons and four-fold-symmetrical InN hierarchical nanostructures by varying the vaporization temperature of $InCl_3$ and deposition temperature. The formation mechanism of the InN nanostructures has been discussed on the basis of the change in $InCl_3$ vapor pressure and the morphological evolution under different temperature. The field emission properties of the InN nanocones were evaluated due to their unique sharp apex geometry, which showed a turn on field of ~12 V/μm, suggesting their potential application in field emission devices.

1. Introduction

Indium nitride (InN) nanostructures have attracted much research interest for their promising applications in infrared light emission and detection [1–4], electric transport [5–7], high output piezoelectric nanogenerators [8,9] and THz radiation [10] originating from the unique properties of InN such as narrow direct band gap (~0.7 eV), high electron mobility, large piezoelectric effect, and surface electron accumulation [11,12]. Accordingly, the facile synthesis of InN nanostructures is of great importance. However, the formation of InN nanostructures suffered the problems of their low growth rate below 500 °C and upward dissociation trend at the temperature higher than 600 °C [13]. Till now, several strategies have been developed for the synthesis of InN nanostructures. Vapor–liquid–solid growth [14–17] of InN nanowires necessitated the assistance of Au or In catalysts, which favored the selective-area deposition but would disturb the (opto)electronic properties of InN nanowires. Plasma-assisted molecular beam epitaxy method [18–20] could yield InN nanocolumn arrays with controllable sizes and could easily regulate their composition by doping, while expensive growth system was required. Metal-organic chemical vapor deposition route [21,22] to InN nanowires commonly used poisonous trimethyl-indium as precursor, which demanded for specialized equipment and safety precautions. Carbonitridation reaction of In_2O_3 and carbon nanotubes in N_2 [23] needed high temperature (>1050 °C) to in situ generate higher pressure of In source, and ammonolysis reaction of In_2O_3 powder [24–26] produced surface-rough InN nanostructures with poor crystallinity in the range of 600–730 °C. It is seen there were some disadvantages existing in these synthetic strategies, and a convenient and catalyst-free method is demanded for the facile synthesis of InN nanomaterials.

Vapor–solid growth through the chemical reaction of $AlCl_3$ and NH_3 has been demonstrated to be an efficient catalyst-free method to yield AlN nanocone arrays [27,28]. The inherent asymmetry of the hexagonal crystal structure of AlN was regarded to be the main reason for the preferential growth of one-dimensional (1D) nanostructures. For growing GaN and InN nanomaterials, MCl_3 (M = Ga, In) was in situ-generated alternatively by converting metal-based precursor with HCl, which reacted with NH_3 to form GaN and InN 1D nanostructures via anisotropic growth [29,30]. In comparison with the alternative route, direct utilizing anhydrate MCl_3 powder as precursor is more convenient, safer and low cost. Recently, this chloride-sourced chemical vapor deposition (CCVD) strategy was applied successfully to synthesize 1D nanostructures of group-III nitrides and their ternary alloys [8,31–33], showing its simple processing and wide generality. Though InN nanorods with sharp ends have been prepared on Si and sapphire substrate by the CCVD

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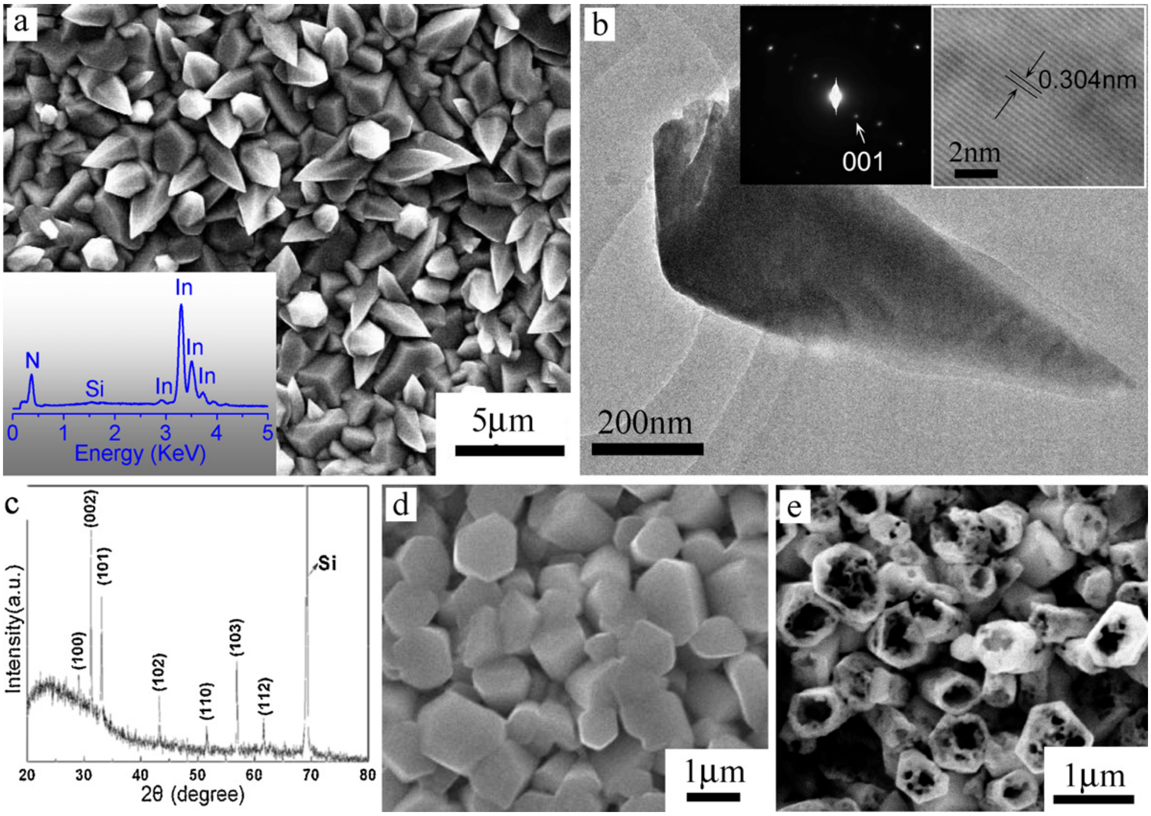

Fig. 1. Characterizations on the InN products obtained at VT = 470 °C. (a) SEM image of the InN nanocones obtained at DT = 550 °C. Inset is the corresponding EDS spectrum. (b) TEM image of an InN nanocone. Insets are the HRTEM image and SAED pattern. (c) XRD pattern of the InN sample in (a). (d)–(e) SEM images of the InN products obtained at DT of 600 and 650 °C, respectively.

method [8,33], the morphological regulation of InN nanostructures has not been studied detailedly yet. Herein we studied the influence of In flux and deposition temperature on the InN nanostructures, and their morphologies were regulated from one-dimensional nanocones and hexagonal nanoprisms to octahedrons and four-fold-symmetrical InN hierarchical nanostructures by varying the vaporization temperature (VT) of $InCl_3$ and deposition temperature (DT) of InN products. Due to the unique sharp tips of InN nanocones, their field emission properties were evaluated, which showed a turn on field of ~12 V/μm, suggesting the potential application of InN nanocones in field emission devices.

2. Experimental

InN nanostructures were synthesized via a CCVD process through chemical reaction of $InCl_3$ and NH_3. Typically, anhydrous $InCl_3$ (99.999%, Aldrich) and unpolished Si substrate were placed separately in a two-zone tubular furnace (see Fig. S1), and then the alumina tube was sealed quickly to avoid the deliquescence of $InCl_3$. After removing O_2 and H_2O by evacuating and Ar flushing for several times, the furnace was heated up under the protection of Ar (99.99%) flow. The temperatures at $InCl_3$ powder and Si substrate were elaborately adjusted in different runs. At the designed temperature, the vaporized $InCl_3$ species was transported by Ar flow (200 mL min^{-1}) to Si substrate, and reacted with NH_3 (200 mL min^{-1}, 99.99%) for about 4 h. The morphologies of InN nanostructures were regulated by changing the VT of $InCl_3$ and DT of InN product. Scanning electron microscopy (SEM, SHIMADZU-SSX-550), equipped with an energy dispersive X-ray spectroscopy (EDS, SHIMADZU-SEDX), was used to characterize the morphologies and component of the products. High-resolution transmission electron microscopy (HRTEM, JEM2100) and X-ray diffraction (XRD, Philips X'pert Pro X-ray diffractometer) were employed to learn the crystalline structure of the products. Field emission measurements were carried out using a parallel-plate diode configuration in a test chamber with the pressure of $\sim 7 \times 10^{-5}$ Pa.

3. Results and discussion

It is generally accepted that the prevailing growth morphology of nanomaterials is highly dependent on the supersaturation level [34]. For the growth of InN nanostructures by CCVD method, the supersaturation degree of InN species produced from the reaction $InCl_3(g) + NH_3(g) \rightarrow InN(s) + 3HCl(g)$ was mainly determined by reaction temperature and vapor pressure of $InCl_3$. The vapor pressure equation for $InCl_3$ is $\lg P(\text{kPa}) = 13.53 - 9074/T(\text{K})$ [35,36], and the corresponding pressure (P)–temperature (T) plot showed its vapor pressure at 470–480 °C was in the range of 20–30 kPa (see Fig. S2), which was potentially suitable for the growth of low-dimensional nanomaterials similar to the case of AlN [37]. Consequently, the VT of $InCl_3$ was set at 470 °C and the DT was changed in the range of 550–650 °C for surveying the influence of DT on the resultant products. At the DT of 550 °C, the product exhibits the conelike morphology with the length of 1–2 μm and the tip diameter less than 5 nm (Fig. 1a). SEM image also reveals that faceted crystals were formed on the Si substrate firstly, on which the nanocones are developed through an epitaxial growth manner. The EDS spectrum (inset in Fig. 1a) indicates the product was composed of In and N elements with a trace of Si from the substrate, in well agreement with the XRD result (Fig. 1c) which manifests the product have the composition of hexagonal InN with the preferential growth direction of [0 0 1]. Fig. 1b displays the TEM image of an individual InN nanocone, which possesses a single crystalline structure grown along c-axis as reflected by the