

Growth of InN films and nanorods by H-MOVPE

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Abstract

InN films and nanorods were grown by hydride metalorganic vapor phase epitaxy (H-MOVPE) and the effects of growth temperature, and NH_3/TMIIn and HCl/TMIIn ratios on morphological dependences were studied. The growth habit of InN varied from thin film to microrod to nanorod to no deposition as the growth conditions were changed about transition from growth to etching conditions. The growth and etch regimes were also predicted by chemical equilibrium calculations of In–C–H–Cl–N-inert system. The optical properties of InN nanorods and columnar structured films were measured by room temperature PL and a maximum intensity was observed at 1.08 eV for both structures.

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1. Introduction

The group III nitrides are now receiving considerable attention as the host semiconductor for optoelectronic and high-power, high-temperature electronic device applications. Among the nitrides, InN has the smallest effective mass and highest electron drift velocity, making it a particularly attractive material for high-speed electronic devices. The growth of one-dimensional (1D) semiconductors such as nanowires (NWs) and nanorods (NRs) holds the promise of improved crystal quality as well as using quantum size effects to adjust the material properties. GaN [1–3] and InN 1D structures [4–6] have been demonstrated using an Au catalyst to promote growth by a vapor–liquid–solid (VLS) mechanism. Closed-spaced vapor transport using pure indium metal or In_2O_3 and ammonia has been used to grow InN nanostructures without an external catalyst [7–10]. It is possible that the liquid In precursor structures self-seed the growth to give a VLS mechanism.

It would be helpful for certain applications to use chemical vapor deposition (CVD) to produce InN nanostructures in a controlled manner. Although the growth of InN 1D structure by conventional metalorganic CVD has rarely been reported, this laboratory has recently reported successful growth of InN nanorods by hydride metalorganic vapor phase epitaxy (H-MOVPE) without incorporating a catalyst or nanotemplate [11]. Previous work that studied the morphology of the deposited material as a function of growth temperature and HCl/TMIIn ratio showed that InN films and nanorods were grown without In inclusion. The material morphology varied from continuous polycrystalline to dense nanorod, with no material growth at low and high deposition temperature [12]. Comparison of growth conditions to the thermodynamic driving force shows that the growth of InN nanorods occurs near zero driving force (i.e., growth–etch transition conditions). Apparently a key feature of H-MOVPE is the reversibility of the chloride deposition chemistry that allows control of the nucleation process by adjusting the Cl/In atomic ratio (i.e., the HCl/TMIIn molar inlet ratio). The detailed mechanism, however, is not understood.

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Another approach to control the thermodynamic driving force is to adjust the H_2 chemical potential through using H_2 as a carrier gas or both the H_2 and N_2 potentials through changing the decomposition extent of ammonia (NH_3) by varying the temperature or NH_3 partial pressure. Chemical equilibrium calculations predict that simply adding H_2 as part of the carrier gas stream will lead to decreased deposition rate [13] while equilibrium predictions indicate that adding NH_3 will increase the growth rate. Experimentally, excess NH_3 reduces the growth rate of InN thin films [14] suggesting that decomposition of NH_3 produces reactive H_2 but the N_2 thus formed becomes inert. As further evidence, a recent in situ ellipsometric study showed that thermal decomposition of InN begins as low as 340 °C in hydrogen, whereas it is stable to 520 °C in nitrogen [15]. It was reported that only a small growth window in temperature and NH_3 /TMIn ratio exists for which InN films can be grown [16]. At low values of NH_3 /TMIn there is very little reactive nitrogen and the growth rate decreases, while at high-temperature thermal decomposition of InN dominates. The effect of input NH_3 /TMIn molar ratio on the growth of InN films has been studied [16–18]. Its influence on InN 1D structures, however, has not been reported since most studies [7–10] used closed spaced vapor transport, in which it is difficult to control the molar ratio. There are a limited number of reports of synthesis of InN nanostructures by CVD [19,20], hydride vapor phase epitaxy (HVPE) [21], and MBE [22–24], which can independently control the inlet molar ratios. Nevertheless, no morphological study by changing process parameters such as N/In and Cl/In ratios, and growth temperature has been reported.

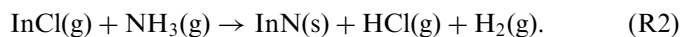
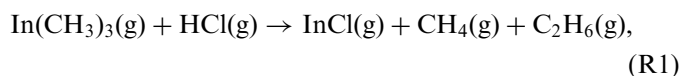
In the present work, InN films and nanorods were grown by H-MOVPE at selected temperatures and values of the NH_3 /TMIn and HCl/TMIn inlet molar ratios. In addition, the boundary between the InN growth and etch regimes was calculated based on chemical equilibrium and the results were compared with experimental data.

2. Experimental

InN films and nanorods were grown on c - Al_2O_3 and Si (1 1 1) by H-MOVPE. This growth method is a variant of the well-established HVPE process, which reacts the pure group III metal with HCl to form the metal chloride (e.g., InCl), and then mixes this with the group V hydride (e.g., NH_3) to deposit the compound semiconductor in a hot wall reactor. H-MOVPE substitutes a gas stream of group III organometallic (e.g., trimethylindium; TMIn) for the condensed metal source (e.g., pure liquid In) to give a more controllable growth process. A more complete description of the H-MOVPE deposition process is presented elsewhere [25].

The indium and nitrogen sources were TMIn (TMI solution, Epichem) and NH_3 (Anhydrous Grade 5, Matheson-Trigas), respectively. The overall reactions of

InN growth reactions are as follows:



Comprehensive studies on the effect of growth temperature and HCl/TMIn ratio on the morphology of films/nanorods were previously reported [12]. The key finding of these studies is that the growth transitioned from a film growth to microstructured to nanostructured surfaces as the thermodynamic driving force transitioned through the growth to etching conditions. In these studies the NH_3 /TMIn ratio was set at 250 and thus the effect of NH_3 /TMIn was not studied. In the present work, the molar ratio of NH_3 /TMIn was varied in the range 100–7000 by changing the NH_3 flow rate (70–4900 sccm). Additionally, two values of the HCl/TMIn were studied (HCl/TMIn = 1 and 4; HCl flow rate = 0.7 and 2.8 sccm, TMIn flow rate = 0.7 sccm) at two growth temperatures (550 and 600 °C) in N_2 carrier gas (N_2 flow rate = 1600 sccm). The growth time was maintained 1 h for all experiments.

3. Results and discussion

It was observed that the morphology of the deposited material changed significantly depending on the values of the NH_3 /TMIn and HCl/TMIn ratios and growth temperature. Representative images of InN nanorods are shown in Fig. 1. At the high temperature (600 °C), high HCl/TMIn (4), and relatively low NH_3 /TMIn ratio (<500), InN nanorods were observed. Nanorods with diameter <100 nm were only observed when the NH_3 /TMIn ratio was lower than 500. Interestingly, the nanorods had a uniform diameter only at a NH_3 /TMIn ratio = 250. The diameter of the all individual nanorods regardless of NH_3 /TMIn, however, was uniform along the growth direction. This suggests that the nucleation process controls the nanorod diameter.

The high Cl/In, high growth temperature, and low N/In conditions are the one with the lowest driving force (i.e., the Cl tends to keep the In in the vapor as the metal chloride and the thermal decomposition is favored at high temperature and low N/In). It is well established that the natural growth habit of GaN is along the c -axis, even on amorphous glass substrates [26]. Thus, it is expected that nuclei formed on sapphire are oriented along the c -axis because that is the most favorable direction. The diameter of nanorods increased with higher N/In ratio (500) suggesting that either larger size nuclei formed or lateral growth occurred. The latter is not likely since the rods show no taper. If there was lateral growth, the sidewalls nearest the substrate would have a longer deposition time than the top section, and taper would be expected.

In contrast, at lower temperature (550 °C) and lower HCl/TMIn (1) and NH_3 /TMIn ratios (<1000), columnar

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