Growth of InN films and nanorods by H-MOVPE

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Available online 27 October 2006

Abstract

InN films and nanorods were grown by hydride metalorganic vapor phase epitaxy (H-MOVPE) and the effects of growth temperature, and NH\(_3\)/TMIn and HCl/TMIn 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.

\(\text{PACS: 78.66.Fd; 78.67.--n; 81.15.Gh} \)

Keywords: InN; Indium nitride; Nanorods; Films; Photoluminescence; Bandgap; H-MOVPE; Thermodynamics; Equilibrium calculation; Morphology

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\(_2\)O\(_3\) 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/TMIn 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/TMIn 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$_2$O$_3$ and Si (111) 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 (TMIn solution, Epichem) and NH$_3$ (Anhydrous Grade 5, Matheson-Trigas), respectively. The overall reactions of InN growth reactions are as follows:

\[
\text{In(CH}_3)_3(g) + \text{HCl(g)} \rightarrow \text{InCl(g)} + \text{CH}_4(g) + \text{C}_2\text{H}_6(g). \quad (\text{R1})
\]

\[
\text{InCl(g)} + \text{NH}_3(g) \rightarrow \text{InN(s)} + \text{HCl(g)} + \text{H}_2(g). \quad (\text{R2})
\]

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
structures rather than 2D films were observed as shown in Fig. 2. At higher NH$_3$/TMIn ratio, in the range 3000–7000 with HCl/TMIn = 1 and growth temperature 550 °C, InN polycrystalline films were grown. The relatively abundant supply of reactive nitrogen offers a less selective growth condition than the lower NH$_3$/TMIn ratio case. The decrease in grain size at higher NH$_3$/TMIn ratio (7000) is consistent with the H$_2$ etching effect from the added NH$_3$ and it matches well with the InN film growth results [16].

To better understand the growth of InN films and nanorods, a complex chemical equilibrium of the analysis In–N–Cl–H–C-inert system was performed. The boundary between the growth and etch regimes for InN deposition was calculated using the ThermoCalc software and the results are shown in Fig. 3 for several values of N/In. All thermochemical data were obtained from the SUB94 database provided in the ThermoCalc software. The base condition was $P = 1$ atm, and elemental input mole fractions, $X$, given by the relationships: $X(C) = 3 \times X(In)$ and $X(H) = 9 \times X(In) + X(Cl) + 3 \times X(N)$ due to $In(CH_3)_3$, HCl, and NH$_3$ were used as the precursors. The atomic ratio $X(Cl)/X(In)$ was varied from 1 to 4 with $X(Inert)/X(In)$ set at 2285. The temperature and N/In atom ratio were varied to determine InN growth and etch conditions.

As shown in Fig. 3a, the growth/etch transition temperature decreases with increasing HCl/TMIn ratio. For values of HCl/TMIn ratio > 1, the added HCl to the system shifts the equilibrium composition towards increasing the amount of InCl$_x$ in the vapor phase, which lowers the transition temperature. As the HCl/TMIn ratio decreases towards unity the Cl is not in large excess but approaches the stoichiometry of the dominant vapor phase In species, InCl. Thus, a small decrease in the HCl/TMIn ratio liberates a relatively higher proportion of the In for participation in growth. For HCl/TMIn ratio less than unity, there is not sufficient Cl to retain most of the In in the vapor phase and In is now available to form InN. The
temperature of the horizontal line for a given N/In ratio is
the thermal decomposition temperature, which increases
with increasing N/In as expected. For comparison the
outcome of multiple growth runs are also shown on this
figure, indicating whether a film or nanorods or no growth
occurred. These data span a range of conditions (HCl/
TMIn ratio from 1 to 7; NH3/TMIn ratio from 100 to
7000, and growth temperature from 400 to 750 °C). The
general trend is consistent with the equilibrium predictions.
Although kinetic limitations likely exist for both growth
and etching, particularly at low temperature, the transition
point occurs when etching and deposition reactions are
in balance and thus might be expected to be better
predicted by equilibrium calculations. There is one outlier
at HCl/TMIn ratio of 4, for which no growth is observed at
conditions well into the growth region. This particular run
was at the lowest temperature (400 °C), and the thermal
cracking of NH3 is very difficult and thus provides little N
for growth [27].

The companion calculation of transition temperature vs.
N/In atomic ratio is shown in Fig. 3b. This calculation
suggests that the transition temperature increases with
increasing ratio to an asymptotic limit. It is noted that
calculation was only performed for three HCl/TMIn ratios,
each greater than unity. Increasing the N level at constant
HCl and TMIn input increases the ability of N to compete
with Cl for the In. Again the conditions of several
experiments and their outcome are provided in this figure.
The general trend is consistent with the experimental
observations, although two outliers exist at lowest experi-
mental temperature (400 °C) presumably a result of low
extent of NH3 decomposition. The good agreement
between the experimental observations and equilibrium
growth/etch transition predictions suggests that operating
near this transition allows fine control of the nucleation
process and thus the opportunity to control the density and
dimensions of the nanostructures. Of course, kinetic
limitations will be present and influence the actual process.
Whether nuclei of InN or some other surface precursor state is the mechanism that initiates the nanorod growth is not clear, nor is the mechanism by which the ‘bulk’ nanorod grows. It is clear from TEM images reported elsewhere [28], that very well faceted, single-crystal nanorods were produced.

The grown InN nanorods and columnar structured films on Si (1 1 1) showed a room temperature PL with maximum emission at 1.08 eV as shown in Fig. 4. The differences between InN columnar structured films and nanorods in optical properties were not substantial since the diameters of the nanorods were too large to show a quantum size effect.

The reported value for the band-gap energy of InN NWs and NRs varies over the large range 0.8–1.9 eV. In one report for example, NRs were grown on Si (1 0 0) by catalytic CVD showed different diameter NRs on different parts of the wafer. In one area 30–50 nm in diameter NRs exhibited a broad RT PL emission peak at 1.85 eV was observed for InN NW arrays grown on anodic alumina membrane using In metal and ammonia [29]. In other reports, band gaps of 0.8 and 0.83 eV were detected by RT PL from 50 to 100 nm InN NWs (synthesized from indium metal and ammonia and thin MOCVD grown films [8]). It should be noted that a high-quality InN film grown on sapphire by MOCVD in our laboratory also showed RT PL at 0.84 eV. In addition, a band gap of 1.1 eV was detected by RT PL from aligned wurtzite polycrystalline InN nanofingers grown on (0 0 0 1) sapphire [30]. The morphology of these nanofingers is similar to that of the columnar films reported in this work. Not only does the experimental data show scatter in the measured band-gap energy, but theoretical calculations resulted also produce different values. For example, the band gap of 1.1 eV was also calculated from single-walled InN nanotubes based on density functional theory [31].

InN NWs synthesized by the nitridation of indium oxide using ammonia, an estimated band gap of ~1.7 eV was reported [10], which is considered further evidence that oxygen is contributing to the higher value of the band-gap energy. At the same time, a strong RT PL broad emission peak at 1.85 eV was observed for InN NW arrays grown on anodic alumina membrane using In metal and ammonia [29]. In other reports, band gaps of 0.8 and 0.83 eV were detected by RT PL from 50 to 100 nm InN NWs (synthesized from indium metal and ammonia and thin MOCVD grown films [8]). It should be noted that a high-quality InN film grown on sapphire by MOCVD in our laboratory also showed RT PL at 0.84 eV. In addition, a band gap of 1.1 eV was detected by RT PL from aligned wurtzite polycrystalline InN nanofingers grown on (0 0 0 1) sapphire [30]. The morphology of these nanofingers is similar to that of the columnar films reported in this work. Not only does the experimental data show scatter in the measured band-gap energy, but theoretical calculations resulted also produce different values. For example, the band gap of 1.1 eV was also calculated from single-walled InN nanotubes based on density functional theory [31]. On the other hand, other calculations showed 0.8–0.9 eV [32] for wurtzite InN. In light of the above summary, the question as to the correct band-gap value of InN remains open and further study is needed.

4. Conclusions

The morphological evolution of InN growth was studied as function of the NH₃/TMIn ratio from 100 to 7000 at two combinations of HCl/TMIn ratio and temperature (1 and 550 °C, and 4 and 600 °C). Growth at the higher temperature produced nanorods with number density and to a lesser extent diameter increasing with increasing NH₃/TMIn ratio. At the lower temperature a columnar growth structure was observed with the grain size decreasing with increasing NH₃/TMIn ratio. Increasing this ratio
provides more N from NH₃ to react with In but the added hydrogen can also decrease the growth rate. Complex chemical equilibrium calculations were performed on the In–C–H–Cl–N-inert (i.e., N₂) gas system to predict conditions at which a transition between InN growth and etching occur. It was found that experimental conditions for growth of InN nanorods are similar to those predicted by the equilibrium analysis. No growth occurred at the low and high ends of growth temperature as a result of very limited NH₃ decomposition at low temperature and InN thermal decomposition at high temperature. The grown InN nanorods and films were characterized by room temperature PL and both showed a maximum intensity at 1.08 eV.

References