On the dynamics in chemical vapor deposition of InN

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ABSTRACT

Epitaxial, nanometer-thin indium nitride (InN) films are considered as promising active layers in various device applications but remains challenging to deposit. We compare the morphological evolution and characterizations of InN films with various growth conditions in chemical vapor deposition (CVD), by both a plasma atomic layer deposition (ALD) approach and a conventional metalorganic CVD approach. Our results, and previous literature, show that a time-resolved precursor supply is highly beneficial for deposition of smooth and continuous InN nanometer-thin films. We show that the time for purging the reactor between the precursor pulses and low deposition temperature are key factors to achieve homogeneous InN. Our study suggests that 320 °C is the upper temperature where the dynamics of the deposition chemistry can be controlled to involve only surface reactions with surface species. The results highlight the promising role of the ALD technique in realizing electronic devices based on nanometer-thin InN layers.
1. INTRODUCTION

III-nitrides (AlN, GaN, and InN) and their alloys are prominent semiconductor materials. AlN and GaN are highly important for optoelectronic applications and form the backbone in modern light emitting diode technology. The revised band gap of InN to 0.7 eV \(^1\) and its high electron mobility \(^2,3\) open up new opportunities; such as IR emitters, sensors \(^4\), solar cells, \(^5\) thin-film transistors \(^6\), and high-electron mobility transistors \(^7\). As all such applications are based on heterostructures with homogeneous coverage of nano-scale active layers, highly controlled InN epitaxy is paramount to realize any application.

The growth of InN is problematic due to its low thermal stability; InN decomposes to In metal and nitrogen gas at about 550 °C. \(^8\) This has also been manifested by its high equilibrium pressure with nitrogen, which has led to attempts at depositing InN at very high nitrogen pressures. \(^9,10,11\) Due to slow decomposition kinetics of ammonia (NH\(_3\)), \(^12\) the most common nitrogen precursor in chemical vapor deposition (CVD), N/In ratios in the order of >10\(^4\) has been used in CVD of InN. \(^13\) Alternative N precursors, such as dimethylhydrazine and tertiarybuthylhydrazine, has been shown ineffective for the growth of InN. \(^14\) More reactive N species can be accessed by using a plasma-assisted approach, which has been adapted in various growth techniques, such as molecule beam epitaxy, \(^15,16,17\) sputtering \(^18\) and metalorganic CVD \(^19\) for the growth of InN.

We have previously hypothesized that steering the deposition chemistry fully to the surface could be an alternative route for low temperature CVD of InN as it could circumvent the problem of the slow kinetics in the gas phase decomposition of NH\(_3\). A CVD approach fully relying on surface chemistry is atomic layer deposition (ALD), which uses a sequential supply of the precursor gases to make the deposition chemistry surface controlled. \(^20\) ALD of InN has been demonstrated using trimethyl indium (TMI) and either nitrogen plasma \(^21,22\) or NH\(_3\) plasma \(^23\), rendering crystalline InN films. ALD of InN has also been demonstrated using
precursors with chelating ligands with In–N bonds, demonstrating polycrystalline\textsuperscript{24} or epitaxial \textit{InN}\textsuperscript{25} with NH\textsubscript{3} plasma. Recently, we demonstrated that epitaxial and homogeneous wurtzite InN film on 4H-SiC substrate with a thickness down to 5 nm can be grown by using plasma ALD at 320\textdegree C,\textsuperscript{26} which has never been reported by other growth techniques. ALD thus seem to be more promising than other techniques to achieve homogeneous, epitaxial, nanometer-thin InN films. However, the understanding of why ALD hold such advantage over conventional thermal CVD is not properly addressed.

Here, we present an experimental study in which we compare the outcomes from ALD and conventional CVD process using TMI and NH\textsubscript{3} for both approaches. Our results demonstrate that nanometer-thin homogenous InN can only be deposited by a time-resolved CVD approach and show that the morphology of InN is heavily controlled by the purge time between the precursor pulses and the surface temperature. In combination with results from the literature on pulse CVD processes for InN, we point to the deposition chemistry dynamics as an important for deposition of InN for potential device applications.

2. METHODS

2.1 InN Deposition by ALD

A Picosun R-200 ALD system was employed to grow InN films using trimethyl indium, In(CH\textsubscript{3})\textsubscript{3} (TMI) and plasma discharges in a NH\textsubscript{3}/Ar gas mixture. A detailed process development can be found in our earlier work.\textsuperscript{23} In this work, 4H-SiC (0001) was used as the substrate, which allows epitaxial growth of InN.\textsuperscript{26} The samples are loaded in the system without a load lock chamber. The plasma is generated within a quartz tube surrounded by a cylindrical RF coil. The heated substrate holder is located approximately 70 cm below the plasma source. N\textsubscript{2} (99.999 \% and further purified by a getter filter) was used as purge gas in the system and as carrier for the TMI (Pegasus Chemicals, Alpha grade). As previously described a fill-empty
pulsing scheme had to be used to get a sufficient flow of TMI in to the deposition chamber.\textsuperscript{23} The NH\textsubscript{3} plasma was ignited using a plasma power of 2800 W and a mixture of 50 sccm NH\textsubscript{3} (99.9990 % and further dried with a getter filter) and 100 sccm Ar (99.9997 % and further purified with a getter filter). Prior to the deposition of InN, the substrates were subjected to a 2-minute plasma exposure with a 100 sccm Ar + 50 sccm N\textsubscript{2} plasma gas mixture ignited by 2800 W, followed by the first ALD cycle after a 10 s N\textsubscript{2} purge. The base line ALD cycle comprises 4 s TMI pulse, 10 s N\textsubscript{2} purge, 12 s plasma exposure using 50 sccm NH\textsubscript{3} + 100 sccm Ar and 2800 W, and 6 s N\textsubscript{2} purge. The deposition temperatures were between 250 and 450 °C while the pressure was kept at 6 mbar for all growth runs.

In some experiments which were done to demonstrate the importance of controlled surface reaction, the purge time between TMI and NH\textsubscript{3} plasma pulses was varied between 0.1 to 8 sec with growth temperature of 320 °C and 400 °C. To facilitate the comparison on the surface morphology of initial deposition stage, 150 ALD cycles (with a nominal thickness of 6 nm at 320 °C) were performed for each condition.

For the sake of simplicity, we will refer to all samples deposited in this manner as samples deposited by ALD, even if the process conditions are such that a self-limiting ALD behavior is not observed.

\subsection*{2.2 InN Deposition by Continuous CVD}

An Aixtron/Epigress horizontal hot-wall MOCVD reactor was used to grow InN for comparison. TMI (SAFC Hitech, Epi-pure grade) and NH\textsubscript{3} (99.9990 % and further dried with a getter filter) were used as the precursors and 4H-SiC (0001) was used as the substrate. The deposition was performed with N\textsubscript{2} (99.999 % and further purified by a getter filter) as process gas between 320 to 450 °C with continuous supply of both precursors for 30 min. The process pressure was kept at 50 mbar. The gas flows where 15 slm N\textsubscript{2}, 2 slm NH\textsubscript{3} and 0.2 sccm In(CH\textsubscript{3})\textsubscript{3},
giving rise to a N/In ratio of 10 000. The flow of TMI and the growth time where set to expose the substrate to the same amount of TMI molecules in both the ALD and CVD experiments.

2.3 Film Characterization

The surface morphologies of the InN samples were studied by high-resolution LEO 1550 Gemini field emission scanning electron microscope (SEM). The crystalline quality, thickness and the macro-scale roughness were characterized by using x-ray diffraction (XRD) (PANalytical X’Pert Pro with a Cu-anode X-ray tube). Grazing-incidence XRD (GIXRD) and symmetric 20-ω and ω-scans were used to study the crystalline quality. The film thickness was determined by analyzing the X-Ray reflectivity (XRR) results. The XRR data was fitted by software PANalytical X’Pert reflectivity using a two-layer model of the InN film and the substrate (InN/substrate).

2.4 Gas Transport Modelling of ALD Reactor

The gas exchange dynamics of the TMI pulse-purge ALD-half cycle at 320 °C and 450 °C was modelled using computational fluid dynamics (CFD) to study the time-dependent concentration of the gaseous species in the TMI precursor pulse in the close vicinity of substrate. The reactor geometry was discretized to a grid of 7 million elements, and the governing equations of mass, momentum, and energy conservation were numerically solved together with the species transport equation using the finite volume solver Ansys Fluent 2020R2 (ANSYS Inc., Canonsburg, PA, USA). An ideal, square-wave pulse was assumed. TMI was assumed to be an ideal gas diluted in the carrier gas. No chemical reactions were considered in the CFD model. Further computational details are given in Supplementary Material.
3. RESULTS AND DISCUSSION

The surface morphologies, from top view SEM, of the resulting materials on SiC grown by both ALD and CVD approaches between 320 and 450 °C are shown in Fig. 1. For the case of ALD which is shown in the upper right parts of Figs. 1a-c, weak but homogeneous particle-like features can be seen on the substrate surface at 320 °C and below (not shown). With increasing temperature, the grain size increases, and the surface coverage decreases, leading to a non-continuous film as illustrated in Fig. 1b. At 450 °C and above (not shown), micro-size droplets/particles are found dominating the surface (Fig. 1c). For the films from continuous CVD, shown in the lower left parts of Figs. 1a-c, barely any surface features are seen on the sample deposited at 320 °C (Fig. 1a). At 400 °C, very low density of nanoparticles can be found on the substrate (Fig. 1b). At 450 °C, separated, hexagonal grains with diameter ranging from a few nm to 50 nm can be observed (Fig. 1c). Note that the dimension of the islands (few tens nm) deposited by CVD at 450 °C is much smaller than the droplets (1-2 μm) found on the sample deposited by ALD at 450 °C.
Crystalline, hexagonal InN can be found by XRD in the samples deposited by ALD as seen from the InN (0002) diffraction peak at 31.3° in Fig. 2a. It should be noted that the satellite peaks in the vicinity of InN (0002), observed in the samples deposited at 320 °C, are thickness-correlated fringes, which can only be seen in heterojunctions with smooth surface and sharp interface. Such thickness fringes disappears in InN grown at higher temperatures due to
higher surface roughness. Despite that the roughness increases with increasing temperature, the stacking coherence of InN crystal was not affected as shown by the ω-scans against the InN(0002) between 320 and 400 °C as seen from the full-width-half-maximum of the InN (0002) peak in ALD deposited films being nearly identical to the SiC substrate, in the range of 20 to 50 arcs (Fig. 2b). For samples grown by ALD at 450 °C, the crystalline quality of InN is notably degraded by showing a broad FWHM of 600 arcs. The additional peaks at 30.58° and 32.93° in the 20-ω scan can be indexed to In₂O₃ and metallic In, respectively. In droplets, as observed in Fig. 1c, have previously been reported during growth of InN under elevated temperatures and In-rich conditions.²⁷ Among the samples deposited by CVD, only the sample deposited at 450 °C show XRD peaks that can be indexed to InN (Fig 2a). The FWHM of the InN (0002) in the ω-scan for the sample deposited by CVD is roughly 350 arcsec (Fig. 2b), which is significantly wider than for films prepared by ALD at lower temperatures in this work, but is comparable to previously reported CVD films.¹³

Figure 2. X-ray diffractograms of (a) symmetric 20-ω scan of InN films deposited on 4H-SiC (0001) by ALD and continuous CVD. The process temperatures of ALD are indicated respectively in the plot. The curves are plotted in log scale and are shifted vertically for visual clarity. (b) ω scan of InN (0002) and SiC (0004) of samples deposited at different temperatures.
The peak shifting of the InN (0002) peak of approximately 0.15° toward smaller diffraction angles with respect to the strain-free InN (0002) at 31.3°, observed for all samples except the one by ALD at 320°C (Fig. 2a), is mostly likely caused by strain from the lattice mismatch to the substrate and defects within the films. We suggest that oxygen could play a significant role for this. Owing to the very oxyphilic nature of In, seen from the standard Gibbs free energy of formation of -831 kJ/mol for In₂O₃ and -105 kJ/mol for InN,²⁸ any residual O in the reactor and post-oxidation from air exposure can result in InOₓNᵧ or even In₂O₃. Peak down-shift with respect to InN (0002) in XRD symmetric scan has been observed for InOₓNᵧ before it turns completely into In₂O₃, which typically forms the cubic structure that is very different from the wurtzite structure of InN.²⁹ According to EDX element mapping (Fig. 3), we note that In, N, O and Si are uniformly distributed for samples deposited at 320 °C by ALD (Fig. 3a) while an aggregation of oxygen together with In and N can be observed for samples deposited at 400 °C by ALD (Fig. 3b). Assuming that the non-c plane surfaces are more favorable for oxygen incorporation in InN, as observed in GaN,³⁰ the scattered small crystal grains seen in the sample deposited at 400 °C, afford a higher surface area leading to enhanced oxygen incorporation and oxidation. We therefore suggest that the shift of the XRD peak in Fig 2a. can be explained by formation of InOₓNᵧ caused by post-deposition air exposure.

**Figure 3.** EDX elemental mapping on samples deposited by ALD at (a) 320 °C and (b) 400 °C. The corresponding elemental mappings indexed in different colors are shown to the right of respective SEM images. The white scale bars correspond to 1μm.
The results in Figs. 1 and 2 shows that the ALD process holds advantages over the conventional continuous CVD for deposition of InN. There are two major differences between the ALD and CVD approaches: the ALD approach uses plasma activation for the ammonia and the time-resolved supply of the precursors. The difference in the film deposition seen in Fig. 1 is likely explained by one or both differences. When a time-resolved precursor supply, with the pulse times used in the ALD approach, was used in the CVD reactor, no film was obtained at any temperature. When the plasma was disabled in our ALD reactor and a thermal ALD process for InN was attempted, no sign of InN deposition could be seen even at 450 °C. On the other hand, with plasma activation of the NH₃ pulse, InN can be deposited even at 180 °C in the ALD reactor, albeit with a reduced deposition rate and crystalline quality. This demonstrates the importance of the plasma activation of the NH₃ pulse. The utilization of plasma, affording more reactive N species, increases the growth rate as well the crystalline quality of InN has previously also been reported in the literature, in both ALD and CVD systems. The plasma activation therefore seems paramount for the InN deposition at low temperature.

In continuous CVD processes, deposition of InN requires higher temperatures than in ALD (Figs. 1 and 2) and is suggested to depend on gas-phase reactions initiated from the adducts formed by mixing TMI and NH₃. Interestingly, pulsed flow of TMI into a continuous flow of NH₃ and a pulses of TMI and NH₃ with slight overlap have been reported to deposit good quality continuous InN films when the thickness exceeded 75 nm. Separating TMI and NH₃ was concluded advantageous for InN deposition in these studies. This separation of TMI and NH₃ should reduce the formation of adducts in the gas-phase and their importance for the deposition chemistry. From these results in the literature, and from our results presented above, we suggest that time is an important parameter which modulates reaction mechanism its dynamics and strongly influences the deposited InN quality.
An ALD process needs to be done at relative low temperature to ensure the stability of the chemisorbed monolayer, and therefore need sufficiently long purge time to eliminate unwanted chemical reactions of physisorbed molecules. As our ALD work presented above was done in a temperature range higher than the typical InN ALD window of 150-300 °C,\textsuperscript{21,22,38-41} and considering the difference in film deposition at different temperatures observed in Figs. 1 and 2, and the thermal stability of TMI, our ALD of InN is likely to involve several In-species. TMI is considered to be stable up to 300 °C. Between 300 and 325 °C, TMI is reported to decompose fractionally to dimethylindium (DMI) and methyl radicals by homolytic cleavage of one In–C bond.\textsuperscript{42}

Excess precursors, reaction by-products and physisorbed surface species should be removed and evacuated by purging the ALD system with inert gas, N\textsubscript{2}, in our experiments. To further study the influence of time, and in the best possible attempt to mimic continuous CVD in our ALD reactor, we did InN ALD experiments with varied purge time. After the TMI pulse and the subsequent purge, the surface is exposed to a NH\textsubscript{3} plasma, which nitridize the surface and immobilize all In species. The surface morphologies of InN ALD grown with different purge times is then a reflection of the behavior of the adsorbed In-species on the surface.

DMI has also been suggested as a stable surface specie in ALD of InN from TMI.\textsuperscript{43} We, therefore, consider DMI as the main chemisorbed In-species on the surface below 325 °C. When 0.1 s purge time is used after the TMI pulse in a 320 °C deposition, a very high density (1.1×10\textsuperscript{11} cm\textsuperscript{-2}) of scattered particles is seen by top-view SEM (Fig. 4a). A longer purge of 2 s results in a reduced density (1.6×10\textsuperscript{10} cm\textsuperscript{-2}) of averagely larger particles (Fig. 4b). With a long purge time of 8 s, a high-density particle-like feature can be seen uniformly on the surface (Fig. 4c). The particle-like surface feature is likely due to a Stranski-Krastanov growth mode where 3D growth takes over after a critical thickness of approximately 1 nm, which has been experimentally verified.\textsuperscript{44} The particle density, particle size and distance between particles can
be used to depict the distribution of adsorbed In-species on the surface, which changes with time, reflecting their mobility. According to our analysis, the average particle size increases from 5 nm to 16 nm (Fig. 4d) and the inter-particle distance also increases significantly (Fig. 4e) by increasing the purge time from 0.1 s to 2 s. The increase in diameter and distance between the particles on the surface with longer purge time is an indication of mobility of the physiosorbed In-species on the surface until they are immobilized by the NH3 plasma. According to the work by Muneshwar and Cadien, an ALD precursor pulse results in physiosorbed species, able to diffuse on the surface before being chemisorbed. With a long purge, all physiosorbed surface species should either chemisorb or desorb from the surface, leaving only chemisorbed In-species for nitridation. The SEM image shown in Fig. 4c reflects the outcome of InN deposition with a long enough purge time to have, presumably, no physiosorbed In-species. It is also interesting to note that the growth per ALD cycle changes with increasing purge time; 0.1 s purge renders 0.22 Å/cycle, 2 s purge renders 0.31 Å/cycle and 8 s purge gives 0.41 Å/cycle, in line with previous findings by Muneshwar and Cadien. This suggests that the surface dynamics, producing chemisorbed species, is of very high importance for the film deposition. According to our analysis (Figs. 4 d and e), the averaged diameter of InN crystal grains is 9 nm. This result is comparable to the value of InN grown by ALD using N2 plasma on GaN surface as reported by Woodward et al. A finite inter distance (smaller than 7 nm) between particles together with high particle density of 7.5×1011 cm−2 indicates that the InN crystal grains are homogeneously distributed on the surface (Fig. 4c).
Figure 4. SEM images of InN grown by ALD using the standard growth conditions with different purge time between TMIn and NH₃ pulses at 320 °C. The purge times were (a) 0.1 s, (b) 2 s and (c) 8 s. The white scale bars correspond to 200 nm in all images. The diameter and nearest neighboring distance of the bright particles in (a-c) were analyzed by using ImageJ. The particle density for each image is also indicated. The statistical results are presented in histograms (d) and (e).

To better illustrate this coupled gas phase-surface dynamics in our ALD process we utilized CFD modelling of the gas exchange in the reactor chamber. Fig. 5 shows how the concentration of In species in the gas phase changes near the surface during the TMI pulse and the following inert gas purge. With a purge time of 0.1 s, the concentration of In species near the surface is only reduced slightly, while a 2 s purge time afford a significant, but not complete removal of In species on the surface and in the chamber. A 2 s purge reduces the concentration to approximately one-eighth of the concentration just after the TMI pulse. This is similar to the reduction in particle density observed between 0.1 s and 2 s purge (Figs. 4b and c). A purge time of 8 s and longer afforded a surface free from In species except those chemisorbed on the surface.
Figure 5. Computational results of TMI concentration before and after the purge started in our growth process. (a) Average concentration over the substrate. The time between -4 to 0 represents the 4 s TMI pulse as indicated by blue shading. The time starting from 0 and afterward refers to the purge step. At 2 s, there is a non-negligible fraction of TMI left, whereas the gas above the substrate is effectively exchanged after 8 s. This is visualized in (b), which shows residual TMI concentration over a cross section of the reactor chamber for different purge times. Note also that the flow field (and hence the required purge time) was relatively unaffected by temperature.

With increasing temperature, the degree of TMI decomposition increases and monomethyl indium (MMI) can form.\textsuperscript{46} MMI can undergo polymerization, forming poly-MMI, which has very low volatility.\textsuperscript{42} The formation of poly-MMI on the surface is not a self-limiting reaction and thus can continuously absorb In-species on to the surface as long as their concentration permits. Any formation of poly-MMI on the surface in an ALD process will therefore lead to formation of large crystal grains or droplets. At 450 °C, the degree of TMI pyrolysis is even higher and the last In–CH\textsubscript{3} bond in MMI can break. This results in elemental In as reported by Jacko et al.\textsuperscript{46} and evidenced in our XRD of films deposited at 450 °C by ALD (Fig. 2a). The reductive environment of the NH\textsubscript{3} plasma makes the formation of InN not favored for elemental, zero valent, In as an oxidation to In(III) is needed for formation of InN. Elemental In is on the other hand easily oxidized upon exposure to air post deposition, resulting in the observation of In\textsubscript{2}O\textsubscript{3} in our XRD (Fig. 2a).
4. CONCLUSION

We show that a time-resolved CVD approach by plasma ALD affords InN films with superior morphology compared to a conventional, continuous CVD approach by standard thermal metalorganic CVD. We show that the key difference between the processes is not only the plasma activation of the ammonia, but also the time-resolved precursor supply and how this is used to control the dynamics of the deposition chemistry. InN with smooth morphology can be obtained by the plasma ALD approach at 320 °C, provided that adequate time is given between the In- and N-precurors, presumably to allow physisorbed surface species to either chemisorb or desorb. We suggest that the detailed surface dynamics of In species is studied in detail by modeling to provide more insights. This study, and previous findings in the literature, demonstrates the importance of using a time-resolved precursor supply in CVD of InN. It should also be noted that the best results in this study were obtained outside the window where the deposition per ALD cycle is constant with temperature, suggesting that a true, self-limiting ALD behavior is not the critical factor, but rather the dynamic precursor supply.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

4. X. Li and X. Liu, Nanoscale 9, 7320 (2017).


