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The Endocyclic Carbon Substituent of Guanidinate and amidinate precursors controlling ALD of InN films

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Abstract

Indium nitride (InN) is an interesting material for future high frequency electronics, due to its high electron mobility. The problematic deposition of InN films currently prevents full exploration of InN based electronics. We present studies of atomic layer deposition (ALD) of InN using In precursors with bidentate ligands forming In–N bonds; tris(*N,N*-dimethyl-*N'*,*N'*-diisopropylguanidinato)indium(III), tris(*N,N'*-diisopropylamidinato)indium(III) and tris(*N,N'*-diisopropylformamidinato)indium(III). These compounds form a series where the size of the substituent in the endocyclic position decreases from –NMe₂, to –Me and to –H, respectively. We show that when the size of the substituent decreases, InN films with higher crystallinity and optical quality, lower roughness and an In/N ratio closer to unity is achieved. From quantum chemical calculations we show that the smaller substituents lead to less steric repulsion and weaker bonds between the ligand and In centre. We propose that these effects render a more favoured surface chemistry for the nitridation step in the ALD cycle which explains the improved film properties.

Introduction

The high electron saturation velocity, small effective electron mass and high electron mobility of indium nitride (InN) makes it a suitable material for high frequency electronics.^{1,2,3} The possibility to integrate InN in existing high electron mobility transistors (HEMTs), currently based on other group 13 nitrides - aluminum nitride (AlN), gallium nitride (GaN) and their alloys, makes InN a key material for future high frequency transistors. However, InN decomposes to In metal and N₂ gas at around 500 °C,⁴ making deposition of InN films challenging with conventional methods. Chemical vapor deposition (CVD) routes to InN typically use trimethyl indium (In(CH₃)₃) and ammonia (NH₃) as precursors. The low upper

temperature tolerated by the InN crystal and the poor thermal reactivity of NH_3 forces InN CVD to use $\text{NH}_3/\text{In}(\text{CH}_3)_3$ in ratios in the order of 100,000.^{5,6} Rather than relying on gas phase reactivity to form more reactive species, a surface controlled CVD approach with time-resolved precursor delivery could be an alternative way to eliminate the high N/In precursor ratios. This approach would rely on surface chemical reactions between gas phase species and chemisorbed surface moieties. If self-limiting surface chemistry is achieved, such an approach would be an atomic layer deposition (ALD) process. ALD of InN has been demonstrated using $\text{In}(\text{CH}_3)_3$ and N_2 plasma^{7,8} or NH_3 plasma⁹, affording InN of high crystalline quality, albeit with significant levels of carbon impurities emanating from the In–C bonds in the $\text{In}(\text{CH}_3)_3$ precursor. Low temperature ALD processes based on precursors with metal-carbon bonds are known to render carbon impurities in the few atomic percent range.¹⁰ It has further been shown that plasma ALD of InN requires very long plasma exposures (on the order of 100 s) to reduce the carbon content down to approximately 3 atomic percent.⁸ This motivates the use of alternative In-precursors without In–C bonds or oxygen atoms as constituents. Herein, we explore homoleptic hexacoordinated In(III) precursors with In–N bonded bidentate ligands for ALD of InN. These molecules - tris(*N,N*-dimethyl-*N',N''*-diisopropylguanidinato)indium(III) (**1**), tris(*N,N'*-diisopropylamidinato)indium(III) (**2**) and tris(*N,N'*-diisopropylformamidinato)indium(III) (**3**) (Figure 1), have all been recently reported as In precursors for ALD of In_2O_3 .^{11,12,13,14,15} We show that the size of the substituent on the endocyclic carbon atom in the ligand backbone has a substantial effect on the film deposition, with the smaller substituents affording films of higher crystalline quality, smoother morphology, lower impurity levels in the deposited InN films and optical properties closer to those reported for bulk InN. We suggest that this is explained by improved surface chemistry when the size of the substituent is reduced.

Figure 1: Hexacoordinated In (III) precursors **1-3** used for the ALD study of InN.

Methods

Film deposition

Film deposition was undertaken in a hot-wall ALD system, Picosun R-200, equipped with a Litmas Remote Inductively Coupled Plasma Source operating at a base pressure of 400 Pa with a continuous flow of N₂ (99.999% and further purified with a getter filter to remove moisture) into the reaction chamber. The films were deposited on Si (100) substrates that were cut into approximately 15 x 15 mm pieces. The substrates were loaded into the chamber without a load-lock chamber and placed onto a heated substrate holder. After loading the substrates, the chamber was baked for 2 hours at 450 °C with a continuous N₂ flow (300 sccm) to minimize oxygen contamination. After baking, the substrates were exposed to 120 s of H₂ plasma (1000 W plasma power using a gas mixture of 100 sccm Ar and 10 sccm H₂) followed by 120 s N₂ plasma (2800 W plasma power using a gas mixture of 80 sccm Ar and 380 sccm N₂) to further remove oxygen and moisture, parts of the native silicon oxide as well as to nitridise the substrate surface. Precursors **1-3** were loaded into a glass vial and placed in a heated stainless-steel bubbler without a dip-tube for the incoming carrier gas. Approximately 0.5 g of precursor was used for 500 ALD cycles. The bubbler temperature was set to 160, 190 and 155 °C for **1**, **2** and **3**, respectively. A flow of N₂ carrier gas was used through the bubbler as the temperature alone was not enough to obtain a sufficient vapor pressure to move the precursor into the reaction chamber. Thermal decomposition of **1** limited the bubbler temperature. A bubbler temperature of 160 °C for **1** is not optimal as it starts to decompose at 120 °C¹⁴, but lower temperatures did not afford film deposition due to insufficient vapor pressure. To circumvent the low vapor pressures of **1** and **2**, a fill-empty approach was employed. This approach has been previously reported⁹, in brief it uses several pulses of In-precursor with first a high, then low flow of carrier gas into the bubbler. This creates a larger pressure gradient between the bubbler and the reaction chamber, which facilitates the movement of the precursor into the reaction chamber. For **1**, 2 pulses were required using the fill-empty process (Table S1). The same fill-empty process was used for **2**, but 5 pulse cycles was required to obtain film deposition, indicative of the slow surface chemistry previously discussed for **2**.¹² The fill-empty process was not required for **3**, however, 3 pulses were required to obtain full surface coverage, again indicative of a slow surface chemistry as previously discussed.¹² The nitrogen source for the film depositions was an Ar/NH₃ (100/75 sccm) gas mixture, which was ignited with a plasma power of 2800 W for

9 s and followed by a 10 s purge. The same plasma parameters were used for all the In precursors unless otherwise stated.

Precursor synthesis

Precursor **1**, **2** and **3** were prepared according to the literature procedures (Scheme 1).^{11,12,13} All manipulations were carried out under a nitrogen atmosphere using standard Schlenk and glovebox techniques. All NMR spectra were measured with Oxford Varian 300 MHz spectrometer. Solvents peaks were used as an internal standard for the ¹H NMR (300 MHz) spectra. All anhydrous solvents were purchased from Sigma-Aldrich™ and further dried with molecular sieves 4Å. InCl₃ (anhydrous, 99.99%) was purchased from Sigma-Aldrich™ and used without further purification. Precursor **1** and **2** were purified by recrystallization from hexanes and **3** by sublimation (90 °C at 0.1 mbar). Previously reported thermogravimetric analysis of **1**, **2**, and **3** showed single step evaporations with onset temperature and residual masses of 175 °C/11.5%¹⁴, 240 °C/0%¹² and 200 °C/0%¹², respectively.

Scheme 1. Synthesis of hexacoordinated In (III) precursors **1-3**.

Film characterization

The crystallinity of deposited films was studied using Grazing Incidence X-ray diffraction (GIXRD) in a PANalytical EMPYREAN MRD XRD with a Cu-anode x-ray tube and 5-axis (x-y-z-v-u) sample stage. PANalytical X'Pert PRO with a Cu-anode tube and Bragg-Brentano HD optics was used for θ -2 θ measurement and X-ray Reflectivity (XRR) mode to measure the thickness of the films. From the XRR measurements the software PANalytical X'Pert reflectivity was used to fit the data using a two-layer model, InN/substrate (Si and GaN). A LEO 1550 Scanning electron microscopy (SEM) with an acceleration energy of 3-20 kV was used to characterize the morphology of the film. SEM was also used for film thickness measurements on cross section samples when the surface roughness made XRR measurements

unreliable. The composition and chemical bonding of the atoms in the film was characterized with a Kratos AXIS Ultra DLD X-ray photoelectron spectroscopy (XPS) equipped with Ar (0.30 eV) sputtering source. CasaXPS software was used to evaluate the data. Gaussian-Laurentius functions and Shirley background were used to fit the experimental XPS data. The Raman spectra were recorded on a micro-Raman setup utilizing 100X objective and 532-nm solid-state laser (Coherent, Sapphire SF 532-150). The laser was focused to $\sim 0.8 \mu\text{m}$ spot on the sample. The power used was below 1 mW to avoid overheating of the sample. The Raman signal was dispersed by a monochromator (Jobin Yvon, HR460) coupled to a CCD camera. With the 1200 grooves/mm grating used in this measurement the resolution was about 3 cm^{-1} . In order to obtain smooth enough spectra to distinguish the weak signal of the InN film from the strong signal of the substrate, 100 subsequent acquisitions by 20 s were acquired for each sample resulting in a total acquisition time of 2000 s per sample. No changes were observed in the spectra during the series indicating that the laser power utilized was sufficiently low to avoid thermal damage.

Computational details

Density functional theory (DFT) calculations were performed for both gas phase and surface reactions and structures. Gas phase calculations were carried out using the Gaussian16 software suite¹⁶. Atomic structures were optimized and harmonic normal mode vibrations were calculated with B3LYP/def2TZVP level of theory together with the D3 version of Grimme's empirical dispersion^{17,18,19}. All structures were verified to have no imaginary frequencies. Enthalpy and Gibbs free energy were calculated at STP (1 atm, 298.15 K). Surface calculations were carried out using the VASP software with optimizers extended by the VTST package.^{20,21,22} The calculations were performed using the generalized gradient approximation (GGA) functional PBE using with the D3 version of Grimme's empirical dispersion, Projector augmented wave (PAW) potentials and a cut-off energy of 700 eV.^{23,24,25} A slab consisting of 4 In₁₆N₁₆ layers with wurtzite (0001) orientation in a cell with dimensions 14.25, 12.34 and 40.40 Å (Figure S1a) was made to model the surface. The lattice parameters were obtained by optimization of bulk lattice parameters and padded with vacuum along the c-direction to ensure separation of the slabs. Dangling bonds on the bottom of the slab were passivated by hydrogen with 0.75 charge and the top of the cell was saturated with NH₂ groups, modelling a probable surface after the NH₃ pulse.²⁶ The slab was optimized with respect to all atomic positions. To model an adsorbed precursor, two hydrogens from neighboring NH₂ were removed and a precursor molecule with two ligands removed was introduced above this site. The structures

where then optimized with the 3 bottom layers of the slab frozen, Figure S1b-d shows the optimized structures.

Results and Discussion

ALD behaviour

Film deposition experiments where the pulse time for **1** was varied showed that the deposition rate saturated at approximately 0.13 Å/cycle for pulse times longer than 3.5 s (Figure 2a). This indicates a self-limiting surface chemistry between **1** and the NH₃ plasma. As pointed out above, the bubbler temperature required for sufficient vapor pressure of **1** is higher than its decomposition point. Decomposition of **1** was observed in the bubbler by the formation of a metallic grey powder after the bubbler had been heated to 160 °C for approximately 9 hours. The ¹H-NMR spectrum of the grey powder suspended in C₆D₆ showed the presence of the same unidentified thermolysis product as previously reported¹¹ (Figure S2). The decomposition of **1** made it difficult to fully establish if saturation was due to self-limiting surface chemistry or limited by its low vapor pressure.

Reducing the size of the substituent on the carbon atom in the endocyclic position of the ligand from –NMe₂ (**1**) to –Me (**2**) increased the volatility and thermal stability of the resulting In precursor.¹² It has also been shown that **2** has slow surface reaction kinetics, which was mitigated by a stop-flow ALD process in the literature.¹² As our ALD reactor does not have this feature, multiple pulses of **2** was used to compensate for the slow kinetics (See supporting information, Table S1). Different pulse sequences of **2** were investigated and the sequence shown in Table S1 was found to be most suited for deposition. It should be noted here that all five pulses of **2** were required to obtain InN film. The length of the last pulse was therefore changed in film deposition experiments where the pulse time of **2** was varied (Figure 2b). It was found that for pulse times longer than 1 s, the growth per cycle (GPC) saturates at ~0.97 Å/cycle, indicating a self-limiting surface chemistry. Figure 2b also shows that 9 s of NH₃ plasma was required to obtain saturated growth chemistry. The temperature dependence of the GPC for **2** shows a narrow plateau between 290-310 °C (Figure 2c), which indicates an unstable precursor or deposited monolayer at higher temperatures. XRR and cross section SEM analysis could not verify film thickness between 200-280 °C and 320-380 °C due to roughness and assumed low growth rate at these temperatures. At temperatures ≥320 °C, **2** starts to

decompose¹² which could be an explanation to why the thickness decreases when the deposition temperature is increased.

Decreasing the size of the endocyclic carbon substituent from –Me (**2**) to –H (**3**), has been shown to render an even more reactive and thermally stable In precursor.¹² A stop flow process was still required for ALD of In₂O₃ using **3**, indicating a slow surface reaction kinetics.¹² Analogous to **2**, multiple pulses of **3** was used to allow the precursor time to react with the surface (Table S1). It was found that 3 pulses were sufficient to obtain surface saturation on the substrate. All three pulses were varied, similarly to **2**, only changes to the last pulse gave different film thicknesses. This again indicates that the last pulse is essential for saturation of the surface using this multiple pulse process. Figure 2c shows how the GPC is dependent on the pulse lengths of **3** and NH₃ plasma. When no last pulse was used (X = 0 in Table S1) the growth rate was 0.27 Å/cycle. When the last pulse was added (X = 1 s), the growth rate increased to 0.4 Å/cycle and saturated at 0.4 Å/s for X ≥ 1 s (Figure 2d). The saturation curve for NH₃ plasma (Figure 2d) shows that at least 9 s of plasma exposure is necessary to saturate the GPC. These results indicate self-limiting surface chemistry for **3** and NH₃ plasma. The dependence of temperature on the GPC (Figure 2e) shows a plateau between 200-280 °C. Higher temperatures resulted in a lower GPC, which is most likely due to desorption of **3** from the surface. For all the saturation curves of **2** and **3**, the reaction temperature was set at 300 °C and 250 °C, respectively. Figure 2f shows the film thickness for deposition using **3** with a different number of ALD cycles. A linear dependence is observed; however, this trend could not be extrapolated to zero film thickness for zero ALD cycles. Instead, the trend line shows zero film thickness at 110 ALD cycles. This indicates a nucleation delay on Si (100) of approximately 110 ALD cycles. If the GPC is calculated considering the nucleation delay of 110 cycles, it would be 0.51 Å/cycle.

Figure 2. a) Saturation curve of **1** under constant conditions of a 13 s NH₃ plasma pulse and deposition temperature of 200 °C. b) the growth per cycle of **2** with different NH₃ plasma pulse times (red) and different pulse times of **2** (black line), both deposited at 300 °C. c) the growth per cycle curve of **2** at different temperatures, with a 9 s NH₃ plasma pulse and the same pulse sequence of **2** as shown in Table S1. Note that XRR and cross section SEM analysis could not verify film thickness between 200-280 °C and 320-380 °C due to roughness and assumed low growth rate at these temperatures. d) the growth per cycle with different pulse times of **3** (last pulse was varied, * in Table S1) at 220 °C with a 9 s NH₃ plasma pulse (black line) and the growth per cycle curve of **3** at different NH₃ plasma pulses and with a 3, 2, 1 s pulse sequence of **3** at 220 °C (red line). e) the growth per cycle curve of **3** at different temperatures with a 3, 2, 1 s pulse sequence of **3** and a 9 s NH₃ plasma pulse. f) The growth behaviour of **3** at 220 °C with number of cycles, with a 9 s NH₃ plasma pulse and same pulse sequence of **3** as shown in Table S1. The red line indicates the linear trend.

Film crystallinity and morphology

Figure 3. a) GIXRD of **1** on Si (100), 13 s NH_3 plasma pulse and 6 s pulse time of **1** deposited at 200 °C, showing crystalline hexagonal InN. The FWHM of the (002) peak was 1.174° b) GIXRD of **2** on Si (100), 9 s NH_3 plasma pulse and same pulse sequence of **2** as shown in Table S2 at 250 °C, showing crystalline hexagonal InN with a preferred orientation along the c-axis. The FWHM of the (002) peak was 0.891° c) GIXRD of **3** on Si (100), 9 s NH_3 plasma pulse and same pulse sequence of **3** as shown in Table S1 at 220 °C, showing crystalline hexagonal InN with a preferred orientation along the c-axis. The FWHM of the (002) peak was 0.660° .

Indium precursors **1-3** all rendered polycrystalline hexagonal InN films (Figure 3). The crystalline quality of the films, as manifested by the intensity of the XRD peaks, increased with decreasing size of the substituent on the endocyclic carbon atom of the ligand backbone. A smaller substituent on the endocyclic carbon in the ligand also turned the film growth to a more preferred orientation along the c-axis (Figure S3). This was seen by the higher intensity together with smaller FWHM of the (002) peak compared to the other XRD peaks in InN films from **3** compared to films from **2**. The 2θ - ω XRD (Figure S4) and GIXRD (Figure 3) measurement of **2** and **3** also indicates that some grains are tilted indicative from the (002) peak being present in both measurements. The significant difference of crystallinity of **1**, in comparison to **2** and

3, can be attributed to the thermal instability of **1**,¹³ which made it difficult to grow thicker films than ~10 nm.

Top view SEM of the films deposited using **1** shows that the film is composed of grains with a significant size variation (Figure 4a). The size variation indicates that the smaller grains are nucleation points for the larger grains. This difference in size is an indication that the film grows in an island growth mode with continuous re-nucleation. Top-view SEM of films deposited using **2** shows a relatively rough film of large grains, with some grains merging to form bigger and more elongated crystalline grains (Figure 4b). Films deposited using **3** show smoother surface with a more coherent grain size (Figure 4c). The coherent grain size distribution indicates that no significant secondary nucleation occurs during growth. In contrast, **1** and **2** have grains with a larger distribution in shape and size, which is indicative of secondary nucleation during growth.²⁷

Thus, the top view SEM, which indicates a more coherent grain size of InN film when the size of the substituent on the endocyclic carbon is reduced, is in line with the increased crystalline quality from XRD FWHM of the (002) peak.

Figure 4. Top-view SEM of a) **1** with 4 s precursor pulse, 9 s NH_3 plasma at 200 °C, b) **2** with 5 s (5* and 1* in Table S1) precursor pulse, 9 s NH_3 plasma pulse deposited at 300 °C, c) **3** with 1 s precursor pulse, 9 s NH_3 pulse deposited at 220 °C.

Chemical composition

As described above, **1** is a poorly functioning In precursor for ALD of InN and only very thin films (10 nm) could be deposited. These films were difficult to analyse by XPS as sputter cleaning of the film surface was not possible. The In 3d_{5/2} was fitted with one In–N peak at 444.4 eV and one In–O peak at 445.4 eV^{28,29,30} (Figure S4). Since sputter cleaning of the film surface could not be performed, the bulk composition of the film could not be obtained. The surface contained 34 at. % In, 27.6 at. % N, 18.3 at. % O and 20.1 at. % C, giving an In/N = 1.23. Presumably, a significant portion of the oxygen and carbon content is due to air exposure prior to XPS analysis and remaining ligand on the surface.

XPS analysis of the bulk of InN films deposited using **2** shows 49.0 at. % In, 45.4 at. % N, 5.6 at. % O and no carbon with an In/N ratio of 1.08. High-resolution XPS spectrum was used to analyse the In 3d_{5/2} and N 1s regions of the InN films. The In 3d_{5/2} region (Figure 5a) could be fitted with peaks at 444.5 eV and 445.6 eV, corresponding to In–N and In–O bonds, respectively. The N 1s region (Figure 5b) was fitted with peaks at 396.7 eV and 397.7 eV, corresponding to N–In and N–O bonds, respectively.^{28,29,30} These results correlates well with previous studies that show a shift of 1 eV between the In–N and In–O peaks of InN.^{28,29,30}

Figure 5. a) High resolution XPS spectra of In 3d_{5/2} for **2** at 250 °C, 9 s NH₃ plasma and the same pulse sequence of **2** as shown in Table S1. b) High resolution XPS spectra of N 1s for **2** at 250 °C, 9 s NH₃ plasma and the same pulse sequence of **2** as shown in Table S1. c) High resolution XPS spectra of In 3d_{5/2} for **3** at 220 °C, 9 s NH₃ plasma and the same pulse sequence of **3** as shown in Table S1. d) High resolution XPS spectra of N 1s for **3** at 250 °C, 9 s NH₃ plasma and the same pulse sequence of **3** as in Table S1. Two sub-peaks were assigned to obtain a good fit for both In 3d_{5/2} and N 1s. The two sub-peaks correspond to In–N and In–O bond.

XPS measurements of InN deposited from **3** after sputter cleaning shows that the films contain 49.1 at. % In, 48.6 at. % N, 2.3 at. % O and no carbon (Figure S5) with an In/N of nearly 1. The high resolution XPS spectrum of the In 3d_{5/2} region (Figure 5c) was fitted with two sub-peaks; the major component at 444.5 eV was assigned to In–N bond and minor component at 445.6 eV assigned to In–O bond. Two sub-peaks were assigned to the high resolution XPS spectrum of the N 1s region (Figure 5d); 396.7 and 397.7 eV peaks assigned to N–In and N–O bond, respectively. These values correlate well with the XPS measurements for **1** and **2**, and with previous XPS measurements of InN_{28,29,30}. As precursors **1-3** do not contain oxygen atoms, the source of the oxygen in the films is believed to be from air exposure of the reaction chamber upon loading the substrate, which is undertaken without a load lock, oxygen containing species formed in the quartz ICP tube during plasma discharge, the native silicon oxide on the substrate or oxidation of the InN upon exposure to air post deposition. Baking the reaction chamber and

substrate etching by hydrogen plasma prior to deposition served to amend the air exposure upon loading substrates and native oxide on the silicon substrate. The NH_3 plasma has previously been studied by optical emission spectroscopy and no optically active oxygen containing species were found.⁹ The significantly higher standard enthalpy of formation for In_2O_3 (−926 kJ/mol) compared to that of InN (−138 kJ/mol) means that oxidation of InN upon air exposure is favoured.³¹ As the films are polycrystalline (Figure 4), oxygen diffusion into the grain boundaries is a likely process³² and thus air exposure post deposition is a possible cause for the oxygen levels in the InN films.

Optical properties

InN films from both **2** (deposited at 300 °C with 9s NH_3 plasma pulse and same precursor pulse sequence as shown in Table S1) and **3** (deposited at 220 °C with 9s NH_3 plasma pulse and same precursor pulse sequence as shown in Table S1) were analysed by Raman spectroscopy using a micro-Raman setup with 532 nm excitation. The spectra obtained are shown in Figure 6 together with a reference spectrum of the Si substrate. The Raman spectra of InN from **2** and **3** (denoted in the figure) shows the $A_1(\text{LO})$ band, which corresponds to wurtzite InN at approximately 586 cm^{-1} .³³ The $A_1(\text{LO})$ band is more distinct in sample **3** compared to sample **2**, which is indicative of a better crystalline quality for films from this run and is in line with the results from XRD and SEM shown above. The position of the $A_1(\text{LO})$ band in InN from **3** is close to its position in bulk InN (586 cm^{-1}), which shows in the spectrum after subtraction of the Si-substrate spectrum (Figure 6b). Conversely, in InN films from **2** the $A_1(\text{LO})$ band is substantially shifted towards lower wavenumbers of ~580 cm^{-1} . This shift indicates a higher tensile strain in the InN film from **2**. The Raman spectra also show a gap mode at 375 cm^{-1} , which has been attributed previously to In vacancies in the InN films.³³ The gap mode is more pronounced in films from **2** in comparison to **3**, which is consistent with the higher oxygen content in its films of **2** as observed by XPS analysis. A higher oxygen content would correlate to N-O bonds, which explains the large In vacancies for **2** in contrast to **3**. The major Raman peak at 521 cm^{-1} and the second order Raman band at 960 cm^{-1} correspond to the Si substrate.³³

Figure 6. a) The Raman spectra of InN from **2** and **3**, as indicated in the figure, together with the reference spectrum of the Si substrate provided for comparison (bottom curve). b) The spectra of the samples after subtraction of the substrate spectrum. For the purpose of subtraction, the spectra are normalized by the second-order band of Si centered around 960 cm^{-1} . This ensures nearly perfect subtractions of all second-order features of the Si spectrum from the spectrum of the samples with InN, but leads to either over- or under subtraction of the first-order Raman Si peak at 521 cm^{-1} . The position of the $A_1(\text{LO})$ mode is denoted, although this mode is apparently red-shifted to about 580 cm^{-1} compared to 586 cm^{-1} in unstrained wurtzite InN crystal. The gap mode at 375 cm^{-1} associated in with In vacancies is also denoted.²² Note the scale change in the upper spectrum in panel (b).

Surface Chemistry

Deposition of InN using this series of precursors revealed that smaller and less electron donating substituents on the endocyclic carbon ($\text{NMe}_2 < \text{Me} < \text{H}$) not only leads to a more volatile and thermally stable precursor, but also an increase in film quality. Given that ALD is a surface chemistry-based deposition technique, the improved crystallinity and optical quality of the InN films deposited with **3**, is most likely explained by an improved surface chemistry over **1** and **2**. Lowering the bulk on the endocyclic carbon from a -Me to -H decreases the steric repulsion between the endocyclic substituent and the exocyclic N-*i*Pr groups, allowing **3** to change its molecular geometry more easily. This would in-turn change the surface kinetics of **3**, allowing it to react with the substrate faster as the bite angle of the ligand would be more acute and thus exposing the metal centre to the surface more upon chemisorption. This was observed when depositing InN with **3**, which required a total of 6 s over three consecutive pulses (3, 2, 1 sec pulse sequence) to saturate the surface. This time was substantially shorter than **1** and **2**, which required pulses totalling 11 s and 15 s, respectively. An increase in surface kinetics for **3** over **2** was also observed in the ALD of In_2O_3 .¹² In addition, as the *i*Pr groups can move away from each other more freely, this would make the deposited monolayer less hydrophobic, providing films that are more uniform with the absorbed precursor (Figure 7). This was shown for **3**, which gave films with smoother morphology in comparison to **1** and **2**.

Moreover, the absorbed precursor would also have less steric repulsion with the surface, which would make the In–N bonds to the surface shorter, stronger and more thermally stable.

Figure 7. Schematics of the suggested improved surface chemistry for a) precursor **3**, showing the decrease in steric and surface repulsion of its *iPr* groups in comparison to b) precursor **2**. This model was originally proposed for ALD of In_2O_3 from **2** and **3**.¹²

Depending on the endocyclic substituent's electron donating/withdrawing ability, the electronics of the ligand system would also be affected. This would change the M–N bonding strength of the precursor, changing its reactivity with the surface and the reactivity of the formed monolayer towards the subsequent NH_3 plasma pulse. This was observed in this InN study, as when the electron donating ability of the endocyclic substituent decreased ($\text{NMe}_2 > \text{Me} > \text{H}$), the film quality increased

To further investigate the surface chemistry of these precursors, density functional theory (DFT) calculations were conducted. The bond dissociation enthalpy for precursors **1–3** were calculated and are shown in Table 1. The results show that **3** has lowest energy for removal of the ligands, reflecting its higher reactivity with the surface in contrast to **1** and **2**. It was also observed for all precursors that the difference in energy required for losing the first two ligands (67–75 kJ/mol) is approximately half that required to lose the third ligand (126–141 kJ/mol). This result suggests that the precursor loses two ligands upon adsorption to give a surface of the mono-ligated In species (shown in Figure 7). Precursor **3** had the lowest energy required to remove the third ligand (510 kJ/mol), showing that the nitridisation chemistry in the ALD process is more favored for **3** over **1** and **2**.

As *iPr* groups are known to undergo β -hydrogen elimination to the metal centre³⁴, the electronic and steric properties would also affect the transfer reactivity of the methine proton ($\text{CH}(\text{CH}_3)_2$) to the indium centre. To investigate this, the reaction free energy of β -hydrogen elimination was calculated for precursors **1–3** in the gas phase. The results show that the free energy for β -

hydrogen elimination was nearly double for **3** (160 kJ/mol) than **1** (84 kJ/mol) and **2** (99 kJ/mol). This suggests that **1** and **2** are most likely to undergo β -hydrogen elimination than **3**, which is consistent with its increased thermal stability. This also agrees with the electron donating ability of the endocyclic substituent, as a lower electron donating ability leads to a less stable hydride during the migration.

Table 1. Bond dissociation enthalpy (kJ/mol) between the ligands and the In-metal centre

Precursor	1 st Ligand	2 nd Ligand	3 rd Ligand
1	337	412	538
2	327	394	535
3	312	382	510

Finally, to investigate the deposited surface, the geometries of each ligand bonded to the In centre was calculated (Table 2). It should be noted that all mono-ligated precursor species are bonded to three nitrogen sites on the surface. The calculations show that all precursors have similar covalent bond lengths (In–N1; **1**: 2.229 Å; **2**: 2.259 Å; **3**: 2.192 Å). However, precursor **3** shows an elongated coordination bond (2.802 Å) in comparison to **1** (2.392 Å) and **2** (2.408 Å). This allows the *i*Pr groups to fold up (**3**: C6–N1–C2: 118.80(9)°; C5–N4–C6: 121.46(4)°) and rotate more freely, decreasing their steric repulsion with other *i*Pr groups and the surface. The elongated coordination bond allows for the ligand of **3** to have a more acute bite angle (53.08(0)°) in contrast with **1** (58.26(2)°) and **2** (57.06(8)°). This in turn affects the covalent bond strength of the ligand (N1–In3) to the In centre for **3** (159 kJ/mol) and was subsequently shown to be the weakest of the series. The lowest binding energy of the covalent bond and elongated coordination bond suggests the In centre is more exposed, making it easier to remove by the subsequent NH₃ pulse.

Table 2. Calculated geometries and bond strengths of mono-ligated In species on the surface

Precursors	In3-N1 (Å)	In3-N4 (Å)	Ligand Bite Angle° N4-In3-N1	Exocyclic Angle 1° C6-N1-C2	Exocyclic Angle 2° C5-N4-C2	In-L Binding Energy (kJ/mol)
1	2.229	2.392	58.26(2)	123.87(9)	126.00(0)	188
2	2.259	2.408	57.06(8)	123.37(1)	127.04(9)	176
3	2.192	2.802	53.08(0)	118.80(9)	121.46(4)	159

Summary and Conclusion

The homoleptic hexacoordinated guanidinate and amidinate precursors **1-3** were investigated as possible In precursors for ALD of InN with NH₃ plasma. All three precursors rendered crystalline InN films on Si(100) with differing quality. The film composition by XPS showed a In/N ratio close to 1 when using **3**. The oxygen content was 5.6 at. % for **2** and 2.3 at. % for **3**, whilst the films had no detectable carbon impurities by XPS. The films grown with all three precursors showed a dominating In–N bond in the In3d_{5/2} and N 1s high-resolution XPS. Raman spectroscopy showed the wurtzite InN A₁(LO) band in films from **2** and **3**, with a smaller peak shift in InN from **3** compared to bulk InN. The thermal stability and volatility of the precursors has previously been shown to increase with decreasing size of the substituent on the endocyclic carbon position of the ligand backbone, from -NMe₂ (**1**), to -Me (**2**), to -H (**3**). We show that the size of the substituent also affects the quality of the deposited InN films as the crystallinity, morphology, In/N ratio and optical properties were improved with the decreasing size of the substituent. We show by quantum chemical modelling that a smaller substituent renders less steric hindrance on the surface allowing a weaker bond between ligand and In centre. We suggest that the lower steric hindrance and weaker bonded ligand can explain the improved film properties and ALD process with smaller substituents.

Supporting Information

Detailed ALD pulse parameters used, XRD (2θ-θ) of **2** and **3**, XPS of **1**, surface model, ¹H-NMR of **1**.

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TOC Graphic

Supporting information

for

The Endocyclic Carbon Substituent of Guanidinate and Amidinate Precursors Controlling ALD of InN Films

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Table S1. Pulse, purge and flow parameters used for 1, 2 and 3.

1			2			3		
Pulse (s)	Purge (s)	Flow (sccm)	Pulse (s)	Purge (s)	Flow (sccm)	Pulse (s)	Purge (s)	Flow (sccm)
5	0.1	500	5	6	500	3	5	100
4*	10	90	4	3	400	2	7	90
			3	4	300	1*	10	90
			2	5	200			
			1*	6	100			

* indicates the pulses that was varied in order to obtain a saturation curve.

Figure S1. Surfaces obtained after optimization. a) Model NH₂ surface, b) adsorbed 1, c) adsorbed 2 and d) adsorbed 3.

Figure S2. The ^1H -NMR spectrum of the grey powder left in the bubbler after deposition with **3**. The powder was dissolved in C_6D_6 .

Figure S3. The 2θ - θ XRD of **2**, same pulse sequence as Table S1, 9s NH_3 plasma pulse deposited at 300 $^\circ\text{C}$ (black) and **3** same pulse sequence as Table S1, 9s NH_3 plasma pulse deposited at 220 $^\circ\text{C}$ (red). Both showing hexagonal InN (002) peak, larger intensity for **3** compared to **2**, indicating a preferred growth along the c -axis.

Figure S4: The high-resolution XPS scan for In 3d_{5/2} (a) and N 1s (b) of an InN film deposited using **1**, same pulse sequence as Table S1, 13s NH₃ plasma pulse deposited at 200 °C. Due to the low thickness of the film, the spectra are recorded without sputter cleaning the film surface.

Figure S5. The high-resolution scan of C 1s for **3** using same pulse sequence as in Table S1 with 9s NH₃ plasma pulse deposited at 220 °C, where a) shows the spectra before and b) after sputtering.