Thermodynamic Analysis of Group-III-Nitride Alloying with Yttrium by Hybrid Chemical Vapor Deposition

Mina Moradnia 1,2,3,†, Sara Pouladi 1,2,3,†, Muhammad Aqib 1,2,3,‡ and Jae-Hyun Ryou 1,2,3,4,5,*

1 Department of Mechanical Engineering, University of Houston, Houston, TX 77204, USA
2 Texas Center for Superconductivity at UH (ReSUH), University of Houston, Houston, TX 77204, USA
3 Advanced Manufacturing Institute (AMI), University of Houston, Houston, TX 77204, USA
4 Department of Electrical and Computer Engineering, University of Houston, Houston, TX 77204, USA
5 Materials Science and Engineering Program, University of Houston, Houston, TX 77204, USA
* Correspondence: jryou@uh.edu
† These authors contributed equally to this work.

Abstract: Group-IIIb-transition-metal-alloyed wurtzite Group-IIIa-nitride (IIIb-IIIa-N) thin films have higher piezoelectric characteristics than binary IIIa-N for a broad range of applications in photonic, electronic, sensing, and energy harvesting systems. We perform theoretical thermodynamic analysis for the deposition and epitaxial growth of Y-alloyed GaN and AlN films by a newly introduced growth technique of hybrid chemical vapor deposition (HybCVD), which can overcome the limitations of the conventional techniques. We investigate the equilibrium vapor pressures in the source zones to determine the dominant precursors of cations for the input of the mixing zone. Then, we study the driving force for the vapor-solid phase reactions of cation precursors in the growth zone to calculate the relationship between the solid composition of Y1−xGa1−xN and Y1−xAl1−xN and the relative amount of input precursors (Y vs. GaCl and AlCl3) in different deposition conditions, such as temperature, V/III precursor input ratio, and H2/inert-gas mixture ratio in the carrier gas. The x composition in YAlN changes nearly linearly with the input ratio of cation precursors regardless of the growth conditions. However, YGaN composition changes non-linearly and is also substantially affected by the conditions. The thermodynamic analysis provides insight into the chemistry involved in the epitaxial growth of IIIa-IIIb-N by the HybCVD, as well as the information for suitable growth conditions, which will guide the way for ongoing experimental efforts on the improvement of piezoelectricity of the lead-free piezoelectric materials.

Keywords: alloying; piezoelectric; HybCVD; thermodynamic calculations; thin film

1. Introduction

Group IIIa-N (III-N) materials, such as aluminum nitride (AlN) and gallium nitride (GaN) thin films, draw increasing attention in piezoelectric applications due to their exceptional properties of high-temperature stability, spontaneous electric polarization, low dielectric permittivity, high sound velocity, efficient transduction, and high stiffness [1–3]. However, the piezoelectric coefficients and the resulting electromechanical coupling factors (κf2) of III-N materials are relatively low compared to those of currently dominant piezoelectric materials, such as lead zirconate titanate (Pb(Zr0.52Ti0.48)O3, PZT) [4].

To address the challenge of relatively low piezoelectric coefficients, ternary Group-IIIb-Nitride (IIIb-N) alloys were proposed. The piezoelectric strain constants d33 and d31 of Group-IIIa-N thin films can be significantly enhanced by the incorporation of Group-IIIb transition metals, such as scandium (Sc) and yttrium (Y), due to the reduction of elastic constants, along with an increase in piezoelectric stress constants (ε33 and ε31), hence the significant increase in κf2. The transition-metal-alloyed wurtzite AlN films were proven to increase their piezoelectric coefficients, while retaining most other beneficial material properties [5–7]. Furthermore, the substitution of the Group-IIIa atoms (Al or
Ga) with a larger Group-IIIb atom (Sc or Y) in III-N increases their wurtzite internal parameter, \( u \) (the length of the metal-nitrogen bond parallel to the c-axis relative to the lattice parameter), which can cause a local distortion in the wurtzite structure toward a layered-hexagonal structure and changes the tensile strain \[8\]. The IIIa-IIIb-N thin films can function as a ferroelectric material, as well as piezoelectric material, due to the presence of a transition metal which causes the induced strain. This strain sufficiently reduces the energy barrier between two polarization states of the III-N wurtzite structure for the ferroelectric polarization switching \[9,10\]. Higher piezoelectric coefficients of IIIa-IIIb-N alloys can extend the applications of the piezoelectric devices in wireless communication \[12\], sensors \[13,14\], mechanical energy harvesting \[15,16\], semiconductor-based ferroelectrics \[10\], and optoelectronics \[17\].

The growth of crystalline IIIa-IIIb-N thin films can be accomplished by different deposition techniques. However, each technique shows drawbacks: compromised crystalline quality and film uniformity control \[18,19\], even for the favorable magnetron sputtering growth technique for these metastable materials \[20\]; low volatility of the metalorganic precursors of transition metals \[9,19\] for metalorganic chemical vapor deposition (MOCVD) \[21\]; the requirement of an extremely high vacuum in a growth chamber and very low growth rates \[22,23\] for molecular beam epitaxy (MBE) \[24\]; and no chemical reaction for transition-metal-chloride to form their nitride for hydride vapor-phase epitaxy (HVPE) \[25\]. To address the econo-technical challenges of the existing growth techniques, we proposed a new growth technique, hybrid chemical vapor deposition (HybCVD), utilizing elemental sources, chloride and hydride, as precursors of the Group-IIIb transition-metal element, Group-IIIa element, and nitrogen, respectively, for the epitaxial growth of ScAlN films \[26\].

This new technique can be further extended to Y-alloyed IIIa-N films with additional advantages. First, an ab-initio calculation estimates the significant enhancement in the piezoelectric strain constant \( d_{33} \) by increasing Y content. The \( d_{33} \) increases by 700% for wurtzite \( Y_xA_{1-x}N \), which is higher than that for \( Sc_xA_{1-x}N \) (by 500%) \[6\]. Therefore, AlN alloying with Y could be better for the improvement of the piezoelectric properties. The piezoelectric coefficients of \( Y_xA_{1-x}N \) (\( x_Y = 0.375 \)) are found to be \( d_{33} = 17.5 \) pC/N, \( d_{15} = -11.07 \) pC/N, and \( d_{31} = -8.65 \) pC/N, which are \( \approx 300\%\), \( \approx 400\%\), and \( \sim \)70% higher than those of AlN, respectively. The dielectric constants \( \varepsilon_{11\text{,} 33} \) slightly increase from \( (3.7, 5.1) \) for AlN to \( (5.3, 5.7) \) for \( Y_{0.375}A_{0.625}N \). Therefore, \( k^2 \) of YAIN \((0 \leq x \leq 0.375)\) can be improved up to \( \sim 650\% \) in relation to that of AlN \[27\]. Second, Y element is cheaper than Sc, which can lower overall material and manufacturing costs. Third, Y-alloyed IIIa-N can be better benefited by the HybCVD. GaN deposition by DC sputtering is very challenging due to the very low melting temperature of Ga \((-86^\circ F)\). The lack of a highly volatile precursor of Y poses a challenge in the MOCVD growth of YAIN and YGaN alloys. Also, clustering was reported in the MOCVD growth by increasing Y vapor pressure in an attempt to achieve higher mole fractions of YN in the alloy. Whereas Leone et al. were able to grow a ScAlN alloy by employing several modifications to the standard MOCVD growth \[17\], the MOCVD growth of the YGaN alloy has not been reported.

In the present work, we theoretically study the thermodynamics of (1) precursor reaction chemistry and (2) solid-phase formation of YGaN and YAIN by the HybCVD with various deposition parameters, including growth temperatures, input V/III ratios, and input carrier gas ratios in different parts of source zones and mixing/growth zones.

2. Materials and Methods

2.1. Group-IIIa (Ga) Source-Zone Calculation

Ga-chloride vapor phases are formed in the source zone of Ga by the reaction between elemental Ga and HCl to estimate the amounts of precursors for Ga, which is the major cation content in the YGaN ternary phase. The equilibrium partial pressures of the chloride species in the source zone are used for the input of Ga precursors in the growth zone. Also, it is often important to control the relative amounts of chloride species to minimize their
attack on quartz (SiO₂), which is a typical material for the growth chamber. With input gases of HCl (reactant), H₂, and inert gas (IG) (for carrier gas), seven gaseous species exist over the Ga metal (HCl, GaCl₃, GaCl₂, GaCl, Ga₂Cl₉, H₂, and IG), and their reactions include:

\[
\text{Ga (s,l) + 3HCl (g) \rightarrow GaCl}_3 (g) + 3/2H_2 (g)
\]  
\[
\text{Ga (s,l) + 2HCl (g) \rightarrow GaCl}_2 (g) + H_2 (g)
\]  
\[
\text{Ga (s,l) + HCl (g) \rightarrow GaCl (g) + 1/2H_2 (g)}
\]  
\[
\text{GaCl}_3 (g) + \text{GaCl}_3 (g) \rightarrow \text{Ga}_2 \text{Cl}_6 (g)
\]

Equilibrium constants of the above reactions (Equations (1)–(4)) are:

\[
K_1 = \frac{p_{\text{GaCl}_3} p_{H_2}^{3/2}}{p_{\text{HCl}}^3}
\]
\[
K_2 = \frac{p_{\text{GaCl}_2} p_{H_2}}{p_{\text{HCl}}^2}
\]
\[
K_3 = \frac{p_{\text{GaCl}} p_{H_2}^{1/2}}{p_{\text{HCl}}}
\]
\[
K_4 = \frac{p_{\text{Ga}_2 \text{Cl}_6}}{p_{\text{GaCl}_3}^2}
\]

where \(p_i\) is the equilibrium partial pressure of each gas in the reaction. The temperature-dependent \(K_i\) values can be determined using NIST-JANAF thermochemical tables and HSC Chemistry software version 6 [28–30]. The total pressure of the source zone, \(P_{\text{total}}\), the sum of seven equilibrium partial pressures is:

\[
P_{\text{total}} = \sum p_i = p_{\text{GaCl}_3} + p_{\text{GaCl}_2} + p_{\text{GaCl}} + p_{\text{Ga}_2 \text{Cl}_6} + p_{\text{HCl}} + p_{H_2} + p_{\text{IG}}
\]

The input partial pressure, \(p_{i}^*\), of three input gases—HCl, H₂, and IG—are related to a ratio of the number of chlorine atoms \(\left(\frac{1}{2}p_{\text{HCl}}\right)\) to the number of hydrogen plus inert gas atoms \(\left(\frac{1}{2}p_{\text{HCl}}^* + p_{H_2}^* + p_{\text{IG}}^*\right)\) and a ratio of the number of hydrogen atoms \(\left(\frac{1}{2}p_{\text{HCl}}^* + p_{H_2}^*\right)\) to the number of hydrogen plus inert gas atoms \(\left(\frac{1}{2}p_{\text{HCl}}^* + p_{H_2}^* + p_{\text{IG}}^*\right)\) in the source-zone system, which is defined by \(C\) and \(H\) in the equations as follow:

\[
C = \frac{1}{2} \frac{p_{\text{HCl}}}{p_{\text{HCl}}^* + p_{H_2}^* + p_{\text{IG}}^*}
\]
\[
H = \frac{1}{2} \frac{p_{H_2}}{p_{\text{HCl}}^* + p_{H_2}^* + p_{\text{IG}}^*}
\]

Considering the mass conservation, the \(C\) and \(H\) do not change as the input number of each atom should be equal to the number of each atom in equilibrium partial pressures of the source zone:

\[
C = \frac{3}{2} \frac{p_{\text{GaCl}_3} + p_{\text{GaCl}_2} + p_{\text{GaCl}} + p_{\text{Ga}_2 \text{Cl}_6}}{p_{\text{HCl}} + p_{H_2} + p_{\text{IG}}}
\]
\[
H = \frac{1}{2} \frac{p_{\text{HCl}} - p_{H_2}}{p_{\text{HCl}} + p_{H_2} + p_{\text{IG}}}
\]
The equilibrium partial pressures of gaseous phases \( p_i \) can be calculated from Equations (5)–(13). The calculation is based on the definition of the input parameters: temperature \( T \), total equilibrium partial pressure \( P_{\text{total}} \), input partial pressure of HCl \( p_{\text{HCl}} \), and input ratio of hydrogen in the carrier gas. The amounts of Ga precursors input are further controlled by adjusting the volume flow rate of total input gases in the Ga source zone.

2.2. Group-IIIa (Al) Source-Zone Calculation

We consider the same definitions and calculations for Al source zone for the growth of YAlN ternary phase, which is described in the earlier report [26]. The major difference between Ga and Al source zones is different chloride precursors as a dominant product carried to the mixing zone. The major chloride product in the Ga source zone is GaCl. However, AlCl\(_3\) should be the main precursor considering system integrity and growth-zone thermodynamics.

2.3. Group-IIIb Transition-Metal (Y) Source-Zone Calculation

Transition-metal-chloride precursors cannot be used for the deposition of transition-metal-alloyed III-N. The Y-chloride precursors can be produced by the following chemical reactions:

\[
\begin{align*}
Y (s,l) + HCl (g) & \rightarrow YCl + 1/2H_2 (g) \quad (14) \\
Y (s,l) + 2HCl (g) & \rightarrow YCl_2 (g) + H_2 (g) \quad (15) \\
Y (s,l) + 3HCl (g) & \rightarrow YCl_3 (g) + 3/2H_2 (g) \quad (16)
\end{align*}
\]

From the Gibbs free energy changes for the chemical reactions in Equations (14)–(16) (Figure S1), the formation of YCl and YCl\(_2\) (Equations (14) and (15)) are not possible in a typical temperature range of the source zone. Only YCl\(_3\) can be produced. However, the Gibbs free energy for the formation of solid YN by the reaction between YCl\(_3\) and NH\(_3\) is positive at typical deposition temperatures (Figure S2):

\[
YCl_3 (g) + NH_3 (g) \rightarrow YN (s) + 3HCl (g) \quad (17)
\]

It is necessary to find an alternative precursor.

The elemental precursor of the transition metal can be provided from the equilibrium vapor phase over its condensed phase. For the Y case, the equilibrium vapor pressure can be controlled in a wide range with the exponential dependence of the vapor pressure by temperature and the high boiling point of the transition metals (Figure S3). When the vapor phase element can be transferred by carrier gases from the source zone to the mixing zone, the amount of Y input precursor in the mixing zone is also controlled by the volume flow rates of carrier gases over the transition metal source.

2.4. Growth-Zone Calculation

The obtained equilibrium partial pressures from each source zone become the input partial pressures in the growth zone. GaCl\(_2\), GaCl\(_3\), and Ga\(_2\)Cl\(_6\) are ignored in the input gases in the growth zone of YGaN due to their extremely low equilibrium vapor pressures from Ga source-zone calculation (Figure S4 and Section 3.1.1). Therefore, 7 gaseous species of Y, GaCl, NH\(_3\), HCl, H\(_2\), IG, and GaCl\(_3\) (as a by-product) are considered. Three possible reactions of these species include:

\[
\begin{align*}
Y (g) + NH_3 (g) & \rightarrow YN (s, alloy) + 3/2H_2 (g) \quad (18) \\
GaCl (g) + NH_3 (g) & \rightarrow GaN (s, alloy) + HCl (g) + H_2 (g) \quad (19) \\
GaCl (g) + 2HCl (g) & \rightarrow GaCl_3 (g) + H_2 (g) \quad (20)
\end{align*}
\]
Equilibrium constants corresponding to the above reactions of Equations (18) to (20) are:

\[ K_5 = \frac{a_{YN} \cdot P_{H_2}^{3/2}}{P_Y \cdot P_{NH_3}} \]  
(21)

\[ K_6 = \frac{a_{GaN} \cdot P_{HCl} \cdot P_{H_2}}{P_{GaCl} \cdot P_{NH_3}} \]  
(22)

\[ K_7 = \frac{P_{H_2} \cdot P_{GaCl_3}}{P_{GaCl} \cdot P_{HCl}^2} \]  
(23)

where \( p_i \) is the equilibrium partial pressure of each gas in the reaction and \( a_{YN} \) and \( a_{GaN} \) are the activities of the binary compounds in the YGaN alloy. The interaction parameter between wurtzite YN and wurtzite GaN, \( \Omega_{YN(wurtzite)-GaN(wurtzite)} \) for the calculation of activities based on a regular solution model, is estimated to be 55,853 cal/mol [31]. Total pressure of the growth zone, \( P_{\text{total}} \), is the sum of equilibrium partial pressures of 7 gases:

\[ P_{\text{total}} = \sum p_i = P_Y + P_{GaCl} + P_{GaCl_3} + P_{NH_3} + P_{HCl} + P_{H_2} + P_{IG} \]  
(24)

Considering the stoichiometric relationship between cation (Y and Ga) and anion (N) in \( Y_xGa_{1-x}N \) formation, the solid phase amount of Y and Ga should be the same as that of N. According to the mass conservation law, the amount of each element in the solid phase is the difference between input partial pressure (\( p_i^\circ \)) and equilibrium partial pressures (\( p_i \)) associated with the element. The amount of Y and Ga in solid is:

\[ P_{GaCl} + P_Y - (P_{GaCl} + P_{GaCl_3} + P_Y) \]  
(25)

The amount of N in solid (\( P_{NH_3} - P_{NH_3} \)) is the same as Equation (25) by the stoichiometry:

\[ P_{GaCl} + P_Y - (P_{GaCl} + P_{GaCl_3} + P_Y) = P_{NH_3} - P_{NH_3} \]  
(26)

Again, the number of Cl and H in input gases should be the same as the number of each atom in equilibrium by mass conservation:

\[ C = \frac{\frac{1}{2} P_{GaCl}}{\frac{2}{3} P_{NH_3} + \frac{1}{2} P_{H_2} + P_{IG}} = \frac{\frac{1}{2} P_{GaCl} + \frac{3}{2} P_{GaCl_3} + \frac{1}{2} P_{HCl}}{\frac{3}{2} P_{NH_3} + \frac{1}{2} P_{HCl} + P_{H_2} + P_{IG}} \]  
(27)

\[ H = \frac{\frac{3}{2} P_{NH_3} + \frac{1}{2} P_{H_2} + P_{IG}}{\frac{3}{2} P_{NH_3} + \frac{1}{2} P_{HCl} + P_{H_2} + P_{IG}} \]  
(28)

We consider 5 input gases, including GaCl, Y, H2, IG (carrier gases), and NH3, excluding GaCl2 and GaCl3 from the Ga source zone for the reason explained earlier. The reaction condition is defined by deposition temperature (T), total pressure (\( P_{\text{total}} \)), input partial pressure of GaCl (\( P_{GaCl} \)), input V/III ratio, and the mixing of hydrogen in the carrier gas. Then, from Equations (21)–(28), equilibrium partial pressures of vapor phases are calculated to estimate the Y composition in the alloy compound of \( Y_xGa_{1-x}N \).

A similar approach is used for YAlN alloys. However, due to the difference in the dominant Group-IIIa precursor (GaCl vs. AlCl3), different possible reactions are considered for 6 gaseous species of Y, AlCl3, NH3, HCl, H2, and IG.

Two possible reactions of these species include:

\[ Y (g) + NH_3 (g) \rightarrow YN (s, alloy) + 3/2H_2 (g) \]  
(29)

\[ AlCl_3 (g) + NH_3 (g) \rightarrow AlN (s, alloy) + 3HCl (g) \]  
(30)
Equilibrium constants corresponding to the above reactions of Equations (29) and (30) are:

\[ K_8 = \frac{a_{YN} P_{Y^{3/2} H_2}}{P_Y P_{NH_3}} \]  

(31)

\[ K_9 = \frac{a_{AlN} P_{HCl}^3}{P_{AlCl_3} P_{NH_3}} \]  

(32)

where \( a_{AlN} \) represents the activities of the binary compounds in the YAlN alloy. The interaction parameter between wurtzite YN and wurtzite AlN, \( \Omega_{YN(wurtzite)-AlN(wurtzite)} \), is estimated to be 77,361 cal/mol. We do not include the formation of Al\(_2\)Cl\(_6\) in our calculation due to its positive Gibbs free energy in typical growth zone temperatures (Figure S5).

3. Results

3.1. Input Precursor Control

Thermodynamic analysis in the source zone provides information on the amount of partial pressure of vapor species in the form of chloride or elemental source for the input of the mixing/growth zone.

3.1.1. Precursor from Ga Source Zone

To evaluate and control the amounts of Ga precursors, the equilibrium partial pressures of reactants and products in the Ga source zone as a function of temperature at a fixed total pressure, \( P_{total} = 1 \text{ atm} \) (no vacuum is necessary), are calculated. The partial pressures of other input gases are \( p_{HCl} = 0.00008 \text{ atm} \) and \( p_{H_2} = 0.0999 \text{ atm} \) with remaining IG. Reactions between Ga and HCl form GaCl, GaCl\(_2\), GaCl\(_3\), and Ga\(_2\)Cl\(_6\). At all the temperature ranges (up to 900 \( ^\circ \text{C} \)) of Ga source zone, GaCl is a dominant species among the chlorides (Figure S4). For instance, at a source-zone temperature of 500 \( ^\circ \text{C} \), the equilibrium partial pressure of GaCl is significantly higher than those of GaCl\(_2\), GaCl\(_3\), and Ga\(_2\)Cl\(_6\) by the order of 10 in magnitude, i.e., \( 10^{-5} \text{ atm} \) (\( p_{GaCl} \)) vs. \( 10^{-14} \text{ atm} \) (\( p_{GaCl_2}, p_{GaCl_3}, \) and \( p_{Ga_2Cl_6} \)). Hence, only GaCl is considered as a precursor of Ga in the growth zone.

For the reaction between Ga chlorides and the chamber wall, the change in the equilibrium constant, \( K_i \), as a function of reciprocal temperature, is negative for all the reactions between different chlorides of Ga and SiO\(_2\) (Figure S6); therefore, there is no concern for the degradation of the chamber wall/liner made of quartz. This is different from the Al source zone, where the accurate control of source-zone temperature is necessary to protect the chamber walls. The temperature of the Al source zone should be maintained lower than \( \sim 550 \text{ }^\circ \text{C} \) to dominantly produce the AlCl\(_3\) and suppress the formation of AlCl, AlCl\(_2\), and Al\(_2\)Cl\(_6\) that react with the chamber liner and walls. The calculated results provide a condition for introducing GaCl as a dominant Ga chloride in the Ga source zone in order to transfer the Group-III element to the mixing/growth zone by the assistance of the carrier gases. The thermodynamic calculation of Al source zone was described in detail in the previous paper on the HybCVD of ScAlN [26].

3.1.2. Precursor from Y Source Zone

A high vapor pressure can be achieved in the transition-metal source (Y) zone (Figure S3), since the boiling temperature of Y is very high at \( \sim 3338 \text{ }^\circ \text{C} \). However, the source-zone temperature is not too high, and it is preferably lower than or similar to the growth-zone temperature. At temperature of \( \sim 1200 \text{ }^\circ \text{C} \), the Y equilibrium vapor pressure is \( 1.95 \times 10^{-8} \text{ atm} \) which is significantly lower than that of GaCl, e.g., \( \sim 10^{-4} \text{ atm} \) at most temperatures (Figure S4). A higher flow rates of carrier gas in the Y source zone may compensate this lower Y equilibrium vapor pressure. However, the difference is too much to be compensated by the flow rate control. Nevertheless, low vapor pressure of Y does not cause a serious issue in the growth of YGaN, which will be discussed in Section 4.2.

The Y reactivity with the source zone components should be considered in their materials selection. Pyrolytic boron nitride (BN), graphite, silicon-carbide (SiC)-coated...
graphite, and alumina (Al2O3) are made of materials that can be used for the Y storage container. Based on thermodynamic calculations of the Gibbs free energy changes of Y reaction with various materials for the container, the best way to prevent any damage to the container is to make the container from SiC-coated graphite or graphite (Figure S7).

3.2. Alloy Composition Control

Previous studies show that the high-quality crystalline structure of YAIN can be achieved at Y composition below ~25% where the complete mixing of YN and AlN in wurtzite structure is stable as the crystallinity degrades in Y2Al1−xN at higher xY [32]. Therefore, in the present study for the thermodynamic calculation of Y2Ga1−xN and Y2Al1−xN thin-film growth, only the conditions that can result in piezoelectric films with lower xY are considered. The amount of input Y precursor with respect to the total amount of input cation precursors, input Y ratio, is defined as one of follows (Equation (33) for YGaN and Equation (34) for YAIN):

\[
R_Y = \frac{p_Y^\circ}{p_{GaCl} + p_Y} \quad \text{(33)}
\]

\[
R_Y = \frac{p_Y^\circ}{p_{AlCl}_3 + p_Y} \quad \text{(34)}
\]

The range of R_Y is limited up to ~0.3 in the calculation of the relationship between the cation precursor input ratios (R_Y) and solid compositions (x_Y) (i.e., the mole fraction of YN in Y2Ga1−xN or Y2Al1−xN), considering the range maintaining the piezoelectric properties of the deposited film.

Alloy composition x_Y in Y2Ga1−xN (or Y2Al1−xN) thin films is studied by changing the relative input amounts of Y and Ga (or Al) precursors. At various R_Y, equilibrium partial vapor pressures of reactants and products are calculated at selected temperatures (T_g), input ratios of Group-V precursor to Group-III precursors including both IIIa and IIIb precursors (V/III ratios), and input carrier-gas mixture ratios (effect of H_2 in the carrier gas). The driving force for the deposition of transitional metal III-N alloy is the difference between input partial pressure (p_i^\circ) and equilibrium partial pressure (p_i) of cation precursors, corresponding to the amount consumed in the vapor-solid reaction. The difference in each cation precursor, i.e., p_Y^\circ − p_Y and p_{GaCl}^\circ − p_{GaCl} − p_{GaCl}_3, determines the relative ratio of Y and Ga in the deposited alloy film. Therefore, the solid composition of Y, x_Y in Y2Ga1−xN film is defined by the following equation:

\[
x_Y = \frac{p_Y^\circ − p_Y}{(p_Y^\circ − p_Y) + (p_{GaCl}^\circ − p_{GaCl} − p_{GaCl}_3)} \quad \text{(35)}
\]

A carrier gas is required to transfer the vapor-phase precursors from the source zones into the mixing and growth zones. This carrier gas should be preferably an inert gas (IG), such as argon (Ar) and/or hydrogen (H_2). While nitrogen (N_2) gas is also a common carrier in CVDs, it should be avoided for Y precursors due to its high tendency to react with Y.

3.2.1. Temperature Effect on YGaN Deposition

Temperature is the most critical growth parameter in the CVD method. Figure 1a shows the changes in the equilibrium partial pressures of p_{GaCl}, p_{GaCl}_3, p_{NH}_3, p_Y, p_{H}_2, p_{HCl}, and p_{IG} as a function of R_Y at various T_g (700–900 °C). The other growth conditions are fixed at p_{H}_2 = 0 Pa (no H_2 in carrier gas), p_{HCl}^\circ = 0.1 Pa, and p_{NH}_3 = 10,000 Pa. Input partial pressures of the Y precursor (Y), p_Y^\circ, and the Ga precursor (GaCl), p_{GaCl}^\circ, are varied at the fixed total input partial pressures of cation (Y and Ga) precursors, p_Y^\circ + p_{GaCl} = p_{III} = 100 Pa. Hence, the V/III ratio is also fixed at 100. The equilibrium partial pressure of Y, p_Y, is lower than that of GaCl, p_{GaCl}, by several orders of magnitude in all the given conditions (Figure 1a). A significantly higher equilibrium constant, K_Y, in Equation (21) than K_G in Equation (22) is in line with this difference. This behavior indicates a higher driving force...
for YN formation than that of GaN in given conditions. Both the amounts of \( p_Y \) and \( p_{GaCl} \) increase with an increase in \( T_g \), i.e., the same trend of driving force with temperature. However, the increments in \( p_{GaCl} \) with higher temperatures are significantly higher than those in \( p_Y \). While the amount of \( p_{GaCl} \) decreases with increasing \( T_g \), the change is marginal as compared to the change in \( p_{GaCl} \). Hence, it cannot make a substantial difference in the driving force of GaN formation. At higher temperatures, therefore, the GaN formation becomes less efficient. Consequently, \( x_Y \) increases with temperature at the same \( R_Y \). Also, the difference is more recognizable with higher \( R_Y \), as shown in Figure 1b. Furthermore, slower growth rates are expected at higher temperatures due to slightly reduced driving forces for both the YN and GaN (Figure S5).

![Figure 1](image-url)

**Figure 1.** (a) Equilibrium partial pressures of carrier gas, reactants, and products in the growth zone of YGaN. (b) Mole fraction of YN, \( x_Y \), in the deposited \( Y_xGa_{1-x}N \) solid film as a function of cation precursor input ratio, \( R_Y \), at various growth temperatures, \( T_g \).

### 3.2.2. Hydrogen Effect on YGaN Deposition

The effect of the input mixture of carrier gases is another factor to be considered. IG and \( H_2 \) are used as carrier gases in conventional CVD processes, and their mixture ratio can affect the deposition of YGaN by participation of \( H_2 \) in the chemical reactions. Especially, \( H_2 \) is the by-product of possible reactions for the formation of YN and GaN (Equations (18)–(20)). Figure 2a shows the changes in equilibrium partial pressures of \( p_{GaCl} \), \( p_{GaCl_3} \), \( p_{NH_3} \), \( p_Y \), \( p_{H_2} \), \( p_{HCl} \), and \( p_{IG} \) as a function of \( R_Y \) at the \( H_2 \) input range of \( p_{H_2}^o = 0-100 \) Pa. The other conditions are fixed at growth temperature \( T_g = 800 \) °C, \( NH_3 \) input partial pressure \( p_{NH_3}^o = 20,000 \) Pa, and \( p_Y^o + p_{GaCl}^o = p_{III}^o = 100 \) Pa. Hence, the \( V/III \) ratio is \( p_{NH_3}^o / (p_Y^o + p_{GaCl}^o) = 200 \). When comparing \( p_Y \) and \( p_{GaCl} \) at varied \( p_{H_2}^o \), both \( p_{GaCl} \) and \( p_Y \) increase with higher \( p_{H_2}^o \), while \( p_{GaCl} \) decreases. Variation of \( p_Y \) is marginal compared to the change of \( p_{GaCl} \) and \( p_{GaCl_3} \). The effect of higher \( p_{GaCl} \) on the driving force of GaN formation is more than that of lower \( p_{GaCl} \), resulting in lower GaN formation. The increments in \( p_{GaCl} \) with higher \( p_{H_2}^o \) are significantly higher than those of \( p_Y \), especially at lower
$R_Y$, which causes higher YN formation, specifically at a lower $R_Y$. The $x_Y$ vs. $R_Y$ changes non-linearly with increasing $p_{H_2}^0$, which shows that even at very low $R_Y$, a minimum $x_Y \approx 0.1$ can be obtained.

![Figure 2](image)

Figure 2. (a). Equilibrium partial pressures of carrier gas, reactants, and products in the growth zone of YGaN. (b). Mole fraction of YN, $x_Y$ in the deposited Y$_x$Ga$_{1-x}$N solid film as a function of cation precursor input ratio, $R_Y$, with different H$_2$ input conditions.

3.2.3. V/III Effect on YGaN Deposition

The V/III ratio is another critical growth parameter in the CVD method. Figure 3a shows the equilibrium partial pressure changes vs. $R_Y$ at different V/III ratios in the range of 100–200 by changing $p_{NH_3}^0 = 10,000–20,000$ Pa. The other conditions are fixed at $T_g = 900$ °C, $p_{GaCl_3}^0 = 100$ Pa, and $p_{H_2}^0 = 0$ Pa. By increasing the V/III ratio, $p_Y$ and $p_{GaCl_3}$ increase and $p_{GaCl}$ decreases. The change in $p_Y$ is marginal as compared to the change in $p_{GaCl}$. The driving force of GaN formation increases in the whole range of $R_Y$, mainly because of $p_{GaCl}$ reduction. Although the increase in $p_{GaCl_3}$ with higher V/III ratio could reduce the GaN formation driving force, its effect on the $x_Y$ is limited as compared to the decrease in $p_{GaCl}$. Therefore, the composition of alloy becomes GaN-rich with the increasing V/III input ratio, as shown in Figure 3b. The change of $x_Y$ in the whole range of $R_Y$ shows the same trend at different V/III ratios. Also, the V/III ratio effect on the composition of YGaN alloy is less significant than the effects of hydrogen in the carrier gas.
of 100‒200 by changing $p_{\text{NH}_3}$

\[
\rho_{\text{NH}_3} = \begin{cases} 
10,000 \text{ Pa} 
\end{cases}
\]

\[
\rho_{\text{NH}_3} = \begin{cases} 
15,000 \text{ Pa} 
\end{cases}
\]

\[
\rho_{\text{NH}_3} = \begin{cases} 
20,000 \text{ Pa} 
\end{cases}
\]

The other parameters are limited as compared to the $Y$ and $H$ partial pressures. Therefore, the composition of alloy becomes GaN

\[
\text{Equilibrium vapor pressures of a representative condition, e.g., } T_g = 1200 \, ^\circ C \text{ with } p_{\text{H}_2} = 0 \text{ Pa, } p_{\text{NH}_3} = 10,000 \text{ Pa, and } p_{\text{III}} = 100 \text{ Pa (V/III ratio = 100), are shown in Figure S8.}
\]

Similar to the case of YGaN, $p_Y$ is the lowest among the species. However, $p_{\text{AlCl}_3}$ in YAIN growth zone is lower than $p_{\text{GaCl}}$ in YGaN growth zone by two orders of magnitude, suggesting stronger driving force of AlN deposition than that of GaN. As a result, the $x_Y$ vs. $R_Y$ relationship in YAIN is more linear than that in YGaN. Furthermore, growth temperatures (Figure 4a), hydrogen mixtures in the carrier gas (Figure 4b), and V/III ratios (Figure 4c) do not have significant effects on the $x_Y$, unlike in the case of YGaN. While fewer substantial changes are observed by different growth conditions, their trends are different from those of YGaN. $x_Y$ slightly decreases with higher $T_g$. Increasing the hydrogen partial pressure does not affect the $x_Y$ in YAIN. Table 1 summarizes the changes in $x_Y$ of $Y_xGa_{1-x}N$ and $Y_xAl_{1-x}N$ depending on different growth parameters. All three parameter changes of YAIN are similar to the ScAlN growth by HybCVD [25].
Similar to the case of YGaN, $p_Y$ is the lowest among the $X_{Y}$ amounts of GaCl input. For example, $X_{Y}$ in $Y_xGa_{1-x}N$ ternary alloys by HybCVD, the driving force of YN formation is significantly higher, and its changes with growth parameters are negligible. Therefore, $X_{Y}$ is mostly determined by the change in the driving force of GaN formation.

The Gibbs free energies for the formation of GaN and GaCl$_3$ become less negative at higher temperatures (Figure S5). At lower temperatures, e.g., $T_g < 700$ °C, the Gibbs free energy of GaCl$_3$ formation is more negative than that of GaN. Therefore, substantial amounts of the $p_{GaCl}$ are consumed for the formation of the by-product GaCl$_3$ (Equation (20)). By increasing $T_g$ up to 1000 °C, the difference in the formation of GaCl$_3$ and GaN becomes less, gaining higher driving force for the solid deposition; however, the driving force of GaN formation is still significantly lower than that of YN formation. Therefore, the solid composition of YGaN is heavily YN-rich even at very low Y precursor input, i.e., $X_Y >> R_Y$. For example, $R_Y = 0.002$ at $T_g = 900$ °C and V/III = 100 without H$_2$ in the carrier gas is calculated to yield $X_Y \approx 0.2$ (Figure S9). This discrepancy is mitigated by increasing $R_Y$, i.e., a lesser amount of GaCl input. For example, $R_Y = 0.3$ results in the solid composition in the range of $X_Y = -0.4$–0.5 (Figures 1b, 2b and 3b). As a result, the relationship of $X_Y$ vs. $R_Y$ in YGaN significantly deviates from the linearity. Furthermore, $X_Y$ increases at higher temperatures.

### Table 1. Change of $X_Y$ in $Y_xGa_{1-x}N$ and $Y_xAl_{1-x}N$ by increase of growth temperature ($T_g$), hydrogen (H$_2$) carrier gas, and V/III input partial pressures.

| $T_g$ ↑ | H$_2$ ↑ | V/III ↑ |
|---------|---------|---------|
| $X_Y$ in $Y_xGa_{1-x}N$ | Increase | Increase | Decrease |
| $X_Y$ in $Y_xAl_{1-x}N$ | Marginal decrease | Nearly same | Marginal decrease |

Upward arrow (↑) is an indication of increasing value of the parameters.

### 4. Discussion

#### 4.1. Effect of Temperature and Hydrogen on YGaN Deposition

For the deposition of $Y_xGa_{1-x}N$ ternary alloys by HybCVD, the driving force of YN formation is significantly higher, and its changes with growth parameters are negligible. Therefore, $X_Y$ is mostly determined by the change in the driving force of GaN formation, which is affected by the equilibrium pressures of both GaCl and GaCl$_3$. The Gibbs free energies for the formation of GaN and GaCl$_3$ become less negative at higher temperatures (Figure S5). At lower temperatures, e.g., $T_g < 700$ °C, the Gibbs free energy of GaCl$_3$ formation is more negative than that of GaN. Therefore, substantial amounts of the $p_{GaCl}$ are consumed for the formation of the by-product GaCl$_3$ (Equation (20)). By increasing $T_g$ up to 1000 °C, the difference in the formation of GaCl$_3$ and GaN becomes less, gaining higher driving force for the solid deposition; however, the driving force of GaN formation is still significantly lower than that of YN formation. Therefore, the solid composition of YGaN is heavily YN-rich even at very low Y precursor input, i.e., $X_Y >> R_Y$. For example, $R_Y = 0.002$ at $T_g = 900$ °C and V/III = 100 without H$_2$ in the carrier gas is calculated to yield $X_Y \approx 0.2$ (Figure S9). This discrepancy is mitigated by increasing $R_Y$, i.e., a lesser amount of GaCl input. For example, $R_Y = 0.3$ results in the solid composition in the range of $X_Y = -0.4$–0.5 (Figures 1b, 2b and 3b). As a result, the relationship of $X_Y$ vs. $R_Y$ in YGaN significantly deviates from the linearity. Furthermore, $X_Y$ increases at higher temperatures.

![Figure 4](image-url)
as a result of decreasing the driving force of GaN formation while nearly the same driving force of YN formation is maintained, as described in Section 3.2.1.

Hydrogen is one of the by-products of the reactions in the growth zone (Equations (18)–(20)), which can reduce the driving force for the formation of both YN and GaN when \( p_{H_2} \) increases. If the equilibrium constants (K) are the same, the effect of increasing \( p_{H_2} \) (the result of increasing \( p_{H_2} \)) is more considerable, i.e., more increase in \( p_Y \) in Equation (21) than \( p_{GaCl} \) in Equation (22) because of the higher power of \( p_{H_2} \). However, \( K_6 \) is much smaller than \( K_8 \), thus being related to less negative Gibbs free energy (Figure S5). Therefore, the change in \( p_{GaCl} \) with a minor change in \( p_{H_2} \) is more sensitive. The increase in \( p_{GaCl} \) (with higher \( p_{H_2} \)) is in competition with the decrease in \( p_{GaCl} \) (Equation (23)). However, the effect of \( p_{GaCl} \) is more than \( p_{GaCl} \), which results in lower driving force for the GaN formation. Therefore, \( x_Y \) increases with more hydrogen in the carrier gas. At lower \( R_Y \), the increase in \( x_Y \) is more prominent. At the lower \( R_Y \), \( p_{GaCl} \) is more sensitive by increasing \( p_{H_2} \) because of relatively high \( a_{GaN} \) in addition to small \( K_6 \) value. As a result, \( p_{GaCl} \) changed more significantly to compensate for the increase in \( p_{H_2} \) which increases \( x_Y \) more considerably at lower \( R_Y \).

4.2. Comparison between YGaN and YAIN Deposition

The change of various deposition conditions shows different effects on the YGaN and YAIN compositions. The \( x_Y \) vs. \( R_Y \) does not follow the same trend for YGaN and YAIN. The dominant precursors of chloride in Al and Ga source zones are AlCl\(_3\) and GaCl, respectively, with different amounts of Cl content, which result in different reactions in the growth zone of YAIN and YGaN. The GaCl precursor involves an additional reaction in the growth zone of YGaN, producing GaCl\(_3\) and hydrogen by-products, and these are compared to YAIN, unlike AlCl\(_3\). \( R_Y-\chi_Y \) relationships in YGaN are non-linear in all the deposition conditions. In contrast, nearly linear \( R_Y-\chi_Y \) relationships are obtained in YAIN. Also, the presence of hydrogen as one of the by-products in the YGaN growth zone increases the \( \chi_Y \) in \( Y_xGa_{1-x}N \) compared to \( \chi_Y \) in \( Y_xAl_{1-x}N \), by reducing the driving force of GaN formation more than that of AlN. An increase in hydrogen in the system has the most substantial effect on the temperature, the Gibbs free energy formation of AlN becomes more negative, while it becomes less negative for GaN formation. Therefore, with higher \( T_S \), \( x_Y \) increases in YGaN, while it decreases in YAIN.

A non-linear \( R_Y-\chi_Y \) relationship in YGaN, resulting in YN-rich alloy formation relative to the input cation precursor ratio, may pose a challenge in the composition control of the film. A small variation in \( R_Y \) could cause a significant change in \( \chi_Y \) (Figure S9). However, it is beneficial considering the huge difference in vapor pressures of GaCl and Y. The vapor pressure of Y in the Y source zone is lower than that of GaCl in the Ga-source zone by the order of four in magnitude, which requires very high-volume flow rates for carrier gas from the Y-source zone to the mixing zone to achieve similar amounts of Ga and Y precursors. It is not necessary to achieve similar amounts, as reasonable target composition for the enhanced piezoelectric properties, e.g., \( x_Y = 0.1-0.2 \), can be achieved even with very limited input of Y precursor, e.g., \( R_Y = 0.0005-0.002 \) (Figure S9). A nearly linear \( R_Y-\chi_Y \) relationship in YAIN requires similar amounts of Al and Y precursor inputs. The vapor pressure of AlCl\(_3\) in the Al-source zone (on the \( 10^{-5} \) atm [25]) is lower than that of GaCl in the Ga-source zone (\( \sim 10^{-4} \) atm), hence the difference between Y and AlCl\(_3\) to be compensated is smaller.

5. Conclusions

In summary, thermodynamic calculations for the epitaxial growth and deposition of Y-alloyed GaN and AlN thin films by HybCVD, using precursors of chloride (GaCl and AlCl\(_3\)), vapor-phase elemental source (Y) and hydride (NH\(_3\)), showed the effects of common growth parameters in CVD on the compositions of Y in the films. For YGaN alloys, the relationship between the input cation precursor ratio, \( R_Y \), and composition, \( x_Y \), was not linear: the \( x_Y \) was always higher than \( R_Y \), indicating significantly higher incorporation
of Y in the film. This characteristic is beneficial in achieving a target composition of the film for desired piezoelectric properties, even with a relatively small input precursor of Y originating from the low equilibrium vapor pressure of the precursor. Also, higher growth temperature (700 °C), more H2 in the carrier gas (0 → 100 Pa), and lower V/III ratio (200 → 100) resulted in higher xY by further decrease in driving force of GaN deposition. In contrast, RY vs. xY was nearly linear for YAlN alloys, and the effects of temperature, carrier gas mixture, and V/III ratio on xY were marginal. This study suggests that the HybCVD technique can be employed for the growth of piezoelectric Y-alloyed GaN and AlN materials.

Supplementary Materials: The following supporting information is available at: https://www.mdpi.com/article/10.3390/nano1224053/s1, Figure S1: Gibbs free energy change of possible chemical reactions between Y and HCl for the formation of Y chlorides; Figure S2: Gibbs free energy change of a reaction between YCl3 and NH3 for the formation of YN; Figure S3: Equilibrium vapor pressure of Y over the condensed phase; Figure S4: Equilibrium partial pressures of gaseous species over Ga metal in the Ga source zone; Figure S5: Gibbs free energy change of reactions between Y and NH3 for the formation of YN, GaCl, and NH3 for the formation of GaN, GaCl, and HCl for the formation of GaCl3, AlCl3, NH3 for the formation of AlN, and AlCl3 for the formation of Al2Cl6, Figure S6: Logarithmic equilibrium constants for various reactions between Ga-chlorides and quartz; Figure S7: Gibbs free energy change of reactions between Y and possible source containers; Figure S8: Equilibrium partial pressures of reactants, products, and carrier gas in the growth zone of YAIN; Figure S9: Mole fraction of YN in deposited YxGa1-xN solid film with very small input cation precursor ratios.

Author Contributions: Conceptualization and methodology, M.M. and J.-H.R.; calculations and results validation, M.M., S.P. and M.A.; data curation, M.M., M.A. and S.P.; writing—original draft preparation, M.M. and S.P.; writing—review and editing, M.M., S.P. and J.-H.R.; visualization, M.M.; M.M. and S.P. equally contributed to the present work. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by the Texas Center for Superconductivity at the University of Houston (TcSUH) and the Advanced Manufacturing Institute at University of Houston.

Institutional Review Board Statement: Not Applicable.

Informed Consent Statement: Not Applicable.

Data Availability Statement: Data presented in this article is available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References
1. Turner, R.C.; Fuierer, P.A.; Newnham, R.E.; Shrout, T.R. Materials for High Temperature Acoustic and Vibration Sensors: A Review. Appl. Acoust. 1994, 41, 299–324. [CrossRef]
2. Schneider, M.; Bittner, A.; Patocka, F.; Stöger-Pollach, M.; Halwax, E.; Schmid, U. Impact of the Surface-near Silicon Substrate Properties on the Microstructure of Sputter-Deposited AlN Thin Films. Appl. Phys. Lett. 2012, 101, 221602. [CrossRef]
3. Deger, C.; Born, E.; Angerer, H.; Ambacher, O.; Stutzmann, M.; Hornsteiner, J.; Riha, E.; Fischerauer, G. Sound Velocity of AlxGa1-xN Thin Films Obtained by Surface Acoustic-Wave Measurements. Appl. Phys. Lett. 1998, 72, 2400–2402. [CrossRef]
4. Dagdeviren, C.; Su, Y.; Joe, P.; Yona, R.; Liu, Y.; Kim, Y.-S.; Huang, Y.; Damadoran, A.R.; Xia, J.; Martin, L.W.; et al. Conformable Amplified Lead Zirconate Titanate Sensors with Enhanced Piezoelectric Response for Cutaneous Pressure Monitoring. Nat. Commun. 2014, 5, 4496. [CrossRef]
5. Akiyama, M.; Kamohara, T.; Kano, K.; Teshigahara, A.; Takeuchi, Y.; Kawahara, N. Enhancement of Piezoelectric Response in Scandium Aluminum Nitride Alloy Thin Films Prepared by Dual Reactive Cospattering. Adv. Mater. 2009, 21, 593–596. [CrossRef]
6. Mayrhofer, P.M.; Riedl, H.; Euchner, H.; Stöger-Pollach, M.; Mayrhofer, P.H.; Bittner, A.; Schmid, U. Microstructure and Piezoelectric Response of YxAl1-xN Thin Films. Acta Mater. 2015, 100, 81–89. [CrossRef]
7. Wingqvist, G.; Tasnádi, F.; Zukauskaite, A.; Birch, J.; Arwin, H.; Hultman, L. Increased Electromechanical Coupling in W–ScxAl1−xN. Appl. Phys. Lett. 2010, 97, 95–98. [CrossRef]
8. Tasnádi, F.; Alling, B.; Högglund, C.; Wingqvist, G.; Birch, J.; Hultman, L.; Abrikosov, I.A. Origin of the Anomalous Piezoelectric Response in Wurtzite Sc₅₋ₓAlₓN Alloys. Phys. Rev. Lett. 2010, 104, 137601. [CrossRef]

9. Zhang, S.; Fu, W.Y.; Holec, D.; Humphreys, C.J.; Moram, M.A. Elastic Constants and Critical Thicknesses of ScGaN and ScAlN. J. Appl. Phys. 2013, 114, 243516. [CrossRef]

10. Fichtner, S.; Wolff, N.; Lofink, F.; Kienle, L.; Wagner, B. AlScN: A III-V Semiconductor Based Ferroelectric. J. Appl. Phys. 2019, 125, 114103. [CrossRef]

11. Koleske, D.D.; Creighton, J.R.; Lee, S.R.; Crawford, M.H.; Thaler, G.; Cross, K.C.; Knapp, J.A. Issues Associated with the Metalorganic Chemical Vapor Deposition of ScGaN and YGaN Alloys; Sandia National Laboratories (SNL): Albuquerque, NM, USA; Livermore, CA, USA, 2009. [CrossRef]

12. Tholander, C.; Birch, J.; Tasnádi, F.; Hultman, L.; Palisaitis, J.; Perssson, P.O.Å.; Jensen, J.; Sandström, P.; Alling, B.; Žukauskaité, A. Ab Initio Calculations and Experimental Study of Piezoelectric YₓIn₁−ₓN Thin Films Deposited Using Reactive Magnetron Sputter Epitaxy. Acta Mater. 2016, 105, 199–206. [CrossRef]

13. Akiyama, M.; Tabaru, T.; Nishikubo, K.; Teshigahara, A.; Kano, K. Preparation of Scandium Aluminum Nitride Thin Films. J. Vac. Sci. Technol. A 2004, 22, 361–365. [CrossRef]

14. Saada, S.; Lakel, S.; Almi, K. Optical, Electronic and Elastic Properties of ScAlN Alloys in WZ and ZB Phases: Prospective Material for Optoelectronics and Solar Cell Applications. Superlattices Microstruct. 2017, 109, 915–926. [CrossRef]

15. Martin, F.; Muralt, P.; Dubois, M.-A.; Pezous, A. Thickness Dependence of the Properties of Highly c-Axis Textured AlN Thin Films. J. Appl. Phys. 2012, 111, 093527. [CrossRef]

16. Akiyama, M.; Tabaru, T.; Nishikubo, K.; Teshigahara, A.; Kano, K. Preparation of Scandium Aluminum Nitride Thin Films by Using Scandium Aluminum Alloy Sputtering Target and Design of Experiments. J. Ceram. Soc. Jpn. 2010, 118, 1166–1169. [CrossRef]

17. Leone, S.; Ligl, J.; Manz, C.; Kirste, L.; Fuchs, T.; Menner, H.; Prescher, M.; Wiegert, J.; Žukauskaitė, A.; Quay, R.; et al. Metal-Organic Chemical Vapor Deposition of Aluminum Scandium Nitride. Phys. Status Solidi—Rapid Res. Lett. 2020, 14, 1900535. [CrossRef]

18. Casamento, J.; Xing, H.G.; Jena, D. Oxygen Incorporation in the Molecular Beam Epitaxy Growth of ScₓGa₁₋ₓN and ScₓAl₁₋ₓN. Phys. Status Solidi Basic Res. 2020, 257, 1900612. [CrossRef]

19. Tress, M.T.; Downey, B.P.; Nepal, N.; Storm, D.F.; Katzer, D.S.; Meyer, D.J. Epitaxial ScAlN Grown by Molecular Beam Epitaxy on GaN and SiC Substrates. Appl. Phys. Lett. 2017, 110, 162104. [CrossRef]

20. Wang, P.; Laleyan, D.A.; Pandey, A.; Sun, Y.; Mi, Z. Molecular Beam Epitaxy and Characterization of Wurtzite ScₓAl₁₋ₓN Thin Films. Appl. Phys. Lett. 2020, 116, 151903. [CrossRef]

21. Koukitu, A.; Kikuchi, J.; Kangawa, Y.; Kumagai, Y. Thermodynamic Analysis of AlGaN HVPE Growth. J. Cryst. Growth 1994, 27, 21–34. [CrossRef]

22. Assali, A.; Laidoudi, F.; Serhane, R.; Kanouni, F.; Mezilet, O. Highly Enhanced Electro-Acoustic Properties of YAIN/Sapphire Based Surface Acoustic Wave Devices for Next Generation of Microelectromechanical Systems. Mater. Today Commun. 2021, 26, 102067. [CrossRef]

23. Chase, M.W. NIST-JANAF Thermochemical Tables, 4th ed.; Journal of Physical and Chemical Reference Data Monographs; Monograph 9 (Part I and Part II); American Institute of Physics: College Park, MD, USA, 1998.

24. Ruzinov, L.P.; Gužanickij, B.S. Ravnovesnye Prevarosenia Metallicheskih Reaktsej; Moskov, Russia, 1975.

25. Knacke, O.; Kubaschewski, O.H.K. Thermochemical Properties of Inorganic Substances, 2nd ed.; Springer: Berlin, Germany, 1991; pp. 1–1113.

26. Stringfellow, G.B. Calculation of Ternary and Quaternary III–V Phase Diagrams. J. Cryst. Growth 1974, 27, 21–34. [CrossRef]

27. Žukauskaitė, A.; Tholander, C.; Palisaitis, J.; Persson, P.O.Å.; Darakchieva, V.; Sedrine, N.B.; Tasnádi, F.; Alling, B.; Birch, J.; Hultman, L. YₓAl₁₋ₓN Thin Films. J. Phys. D Appl. Phys. 2012, 45, 422001. [CrossRef]