Surface kinetics in AlN growth: A universal model for the control of surface morphology in III-nitrides

Isaac Bryan^{1*}, Zachary Bryan¹, Seiji Mita², Anthony Rice¹, James Tweedie³, Ramón Collazo¹, and Zlatko Sitar¹

¹ Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA

² HexaTech, Inc., 991 Aviation Pkwy., Suite 800, Morrisville, NC 27560, USA

³ Adroit Materials, 2054 Kildaire Farm Rd., Suite 205, Cary, NC 27518, USA

*Email: isbryan@ncsu.edu

Abstract

AlN epitaxial thin films were grown on both vicinal (0001)-oriented native single crystal AlN substrates and AlN templates grown on vicinal (0001)-oriented sapphire to develop a surface kinetic framework for the control of surface morphology. A Burton, Cabrera, and Frank (BCF) theory-based model is formulated and utilized to understand the dependence of the surface kinetics on the vapor supersaturation, σ , and substrate misorientation angle, α . The surface energy of the Al-polar surface of AlN was experimentally determined using BCF theory to be $149 \pm 8 \text{ meV}/\text{\AA}^2$. The critical misorientation angle for the onset of step-bunching was determined to be $\sim 0.25^\circ$ for a growth rate of 500 nm/hr and temperature of 1250°C. Transitioning from a surface with 2D nuclei to one with bilayer steps required a decrease in σ or an increase in α , whereas the suppression of step-bunching required an increase in σ or a decrease in α .

Keywords: A3. Metalorganic chemical vapor deposition; B1. Nitrides; A1. Growth models; A1. Surface kinetics

I. Introduction

AlN-based AlGaIn technology offers a great potential for deep-UV optoelectronic and high-power electronic devices.^{1, 2} In order to realize such devices, high quality epitaxial films with controlled surface morphology are necessary. While the use of a high crystalline quality native AlN substrate is essential to achieve low dislocation density AlN and Al-rich AlGaIn device layers,³ it is also crucial to obtain and maintain atomically smooth surfaces during the growth to enable growth of compositionally uniform AlGaIn thin films, well-defined quantum well structures with high quantum efficiencies,⁴ and sharp interfaces that enable efficient electron transport in high electron mobility transistors.⁵ The importance of thickness uniformity on the atomic scale has been demonstrated in resonant tunneling devices, such as resonant tunneling diodes and quantum cascade lasers, where the non-uniformity caused by macro steps hindered the overall performance of such devices.^{6, 7} For these reasons, the surface morphology and roughness of epitaxial films is crucial to any device work and must be controlled. The only way to do this is through an understanding of the fundamental surface properties of the materials involved during growth.

It is known that different substrate misorientations and growth modes will result in characteristically rough or smooth surfaces in other material systems, such as GaAs and SiC.^{8, 9} These material systems have been thoroughly investigated in terms of their surface kinetic properties using the well-known Burton, Cabrera, and Frank (BCF) theory of crystal growth.¹⁰ The surface kinetics of adatoms in the vapor phase epitaxial growth on vicinal AlN surfaces has not yet been studied. The effect of substrate misorientation on surface morphology has been observed for AlN and AlGaIn epitaxy on sapphire substrates.^{11, 12} However, kinetics on these surfaces is controlled primarily by the spiral growth due to high dislocation density ($10^9 - 10^{10}$

cm⁻²). The spiral growth coupled with high spiral density makes it difficult to directly observe the long-range surface kinetics as related to different growth modes. Furthermore, the spiral-mediated growth introduces additional roughness that must be mitigated.

Epitaxial growth on the native bulk AlN substrates is still a developing field of study, primarily due to the availability and size of appropriately polished substrates.^{3, 13-17} Even though first devices have been demonstrated on these bulk AlN substrates, a comprehensive understanding of how growth proceeds on their surfaces is still lacking.^{18, 19} In particular, the substrate polishing process must result in a surface that is atomically smooth, properly passivated (to ensure longer term stability), free of subsurface polishing damage, flat (surface and lattice radius of curvature >10 m for a 1" substrate), and oriented to the desired plane with an accuracy of ~ 0.1°.

This report ascertains the importance of the last two mentioned requirements and builds upon the work of Dalmau et al., Rice et al., and Bryan et al.^{3, 13, 15} Rice et al. demonstrated the importance of chemo-mechanical polishing of the substrate for the epitaxial film growth and developed a surface preparation technique for reducing the amount of surface hydroxide on the substrate surface.^{3, 13} The effect of substrate subsurface polishing damage on the epitaxial films was studied by Bryan et al., who explained its connection to the formation of micro-cracks and nano-pits.¹⁵ Furthermore, by growing on a low dislocation density native AlN substrate free of polishing damage, well-defined bilayer steps could be observed, which were free of step pinning by dislocations.^{15, 16} This observation made these surfaces ideal to study fundamental surface kinetics concepts and use them for control of step and terrace morphology, which is a prerequisite for obtaining sharp hetero-interfaces and for control of ternary alloys grown upon these surfaces.¹²

For this study, Al-polar AlN films were deposited by metalorganic chemical vapor deposition (MOCVD) on vicinal c-plane AlN and sapphire substrates. The end result of this study was a practical, predictive framework for controlling the surface morphology of AlN during MOCVD growth. This control was achieved by managing the adatom diffusion length relative to the surface terrace width. This framework was instrumental in predicting the needed process change to transition between 3D growth, step flow, and step bunching.

II. Experimental Procedure

The AlN substrates used in this study were processed from single crystalline AlN boules grown by physical vapor transport.²⁰⁻²² All of the AlN substrates were nominally (0001)-oriented and were obtained from HexaTech with a chemo-mechanically polished, atomically smooth surface, free of surface defects, such as scratches or pits, based on inspection by optical and atomic force microscopy (AFM). The substrates had average dislocation densities $<10^3 \text{ cm}^{-2}$. Before the epilayer growth, the AlN substrates were put through a treatment procedure similar to the one presented by Rice et al.¹³ The treatment began with cleaning the substrates using organic solvents. After cleaning, a wet etch using a 3:1 sulfuric:phosphoric acid mixture was implemented to reduce the amount of surface oxide and hydroxide. The substrates were then loaded into an RF-heated, vertical, cold-walled, MOCVD reactor and ramped to 1100°C with 45 mmol/min flow of ammonia (NH_3) at a total pressure of 20 Torr.

The growth of AlN on sapphire substrates required multiple steps to account for the large lattice mismatch between the substrate and film. First, the sapphire substrates were annealed at 1100°C under vacuum of around 10^{-6} Torr. This was followed by H_2 annealing and nitridation as described elsewhere.²³ A 10 nm, low-temperature AlN buffer layer was deposited at 640°C and annealed at 1050°C in order to control the polarity and morphology of the film. Next, an

intermediate high temperature AlN layer was deposited using a growth condition that promoted 3D growth. The 3D growth led to annihilation of dislocations by dislocation bending towards the inclined free surfaces. This intermediate AlN layer reduced the dislocation density to $\sim 1 \times 10^{10} \text{ cm}^{-2}$ and allowed for thicker films to be realized without cracking. Finally, the growth conditions were changed to promote step flow growth, which provided an AlN/sapphire template with an RMS roughness of between 100 and 200 pm for $5 \times 5 \text{ } \mu\text{m}^2$ AFM scan areas, for the subsequent AlN growth.

All of the samples studied here had final layers that were either deposited on the AlN templates on sapphire or on the native AlN substrates. The growth parameters for the final layers, whose surfaces were studied, are subsequently described. A pressure of 20 Torr was maintained during the entire epilayer growth and H_2 was used as a diluent gas with a flow of approximately 450 mmol/min. Trimethylaluminum (TMA) and NH_3 were used as the Al and N precursors, respectively. The NH_3 flow was fixed at 13 mmol/min while the TMA flow was varied from 7 to 28 $\mu\text{mol/min}$. A TMA flow of 7 $\mu\text{mol/min}$ during AlN growth resulted in a growth rate of about 500 nm/hr. The AlN epitaxial films were grown at temperatures between 1050 and 1250°C. The growth was mass transport limited for all the above conditions.

The quality of epilayers was ascertained using high-resolution x-ray diffraction (HRXRD). For the HRXRD measurements, a Philips X'Pert Materials Research Diffractometer with a $\text{Cu } K_\alpha$ x-ray source was used. The epitaxial layers and substrates were characterized for extended defects by conventional transmission electron microscopy and x-ray topography.²⁴ The surface morphology was characterized using an Asylum Research MFP-3D atomic force microscope in tapping mode. Before growth, both AlN and sapphire substrate surfaces were characterized by AFM. The step height to terrace width ratio was used to determine the

misorientation angle relative to the [0001] direction. These measurements were further supported using standard HRXRD techniques.

III. Results and Discussion

It is well known that for smooth surface morphology, the step flow growth mode is necessary. This growth mode typically requires the presence of terraces with a width on the order of the diffusion length of the adatoms on the growing surface. The two primary sources of steps are screw dislocations and an intentionally misoriented substrate. When the screw dislocation density is very low, as in the case of epitaxial films deposited on native AlN substrates, the surface kinetics is determined by the growth condition and the step density caused by the intentional misorientation of the substrate. No V-defect pitting, step pinning, or spiral growth exists in this case. Figure 1 shows the six primary types of surface morphologies observed in this study for AlN homoepitaxial layers grown on native AlN single crystal substrates.

Figure 1 (a) represents growth on an on-axis AlN substrate that offered large, atomically smooth terraces. Due to large distances to the nearest steps, 2D nuclei formed on these surfaces that grew into epitaxial 3D islands. The 2D nuclei were triangular in shape with steps perpendicular to the $\langle 1-100 \rangle$ directions and rotated by 60° between the neighboring terraces of a single bilayer height of $\sim 2.5 \text{ \AA}$ (or $c/2$). The sample in Figure 1 (b) contained bilayer steps that were closer together than in Figure 1 (a) but separated enough so that 2D nucleation on the terraces was still favorable. Here, the 60° rotation of the 2D nuclei was clearly visible from one bilayer step to the next. The surface in Figure 1 (c) consisted of closely spaced bilayer steps ($c/2$) that yielded an RMS roughness of less than 50 pm. Figures 1 (e) and (f) show step-bunched morphologies where the step heights are many times greater than the bilayer height. The edges of the step-bunches in Figure 1 (e) were predominantly straight as compared to the jagged step-

bunch edges in Figure 1 (f). This difference was found to be due to the differences in the misorientation direction. Samples in Figures 1 (e) and (f) were misoriented toward the $[1-100]$ and $[11-20]$ directions, respectively. In fact, the degree of jaggedness was directly correlated to the deviation of the misorientation direction from the $\langle 1-100 \rangle$ directions and reached a maximum for the offcuts toward the $\langle 11-20 \rangle$ directions, as all steps decomposed into steps pointing in $\langle 1-100 \rangle$ directions. This observation was consistent with observations in Figures 1 (a) and (b), where it was found that the stable steps were $\langle 1-100 \rangle$ -oriented. Finally, Figure 1 (d) represents a meandering step morphology, which was a transitional stage between the bilayer and step-bunched morphologies.

A. Surface Kinetic Theory

To be able to explain and predict surface morphology during growth, a surface diffusion model using BCF theory was considered.¹⁰ For the case of an ideal step, each step is considered to be isotropic in nature, free of nuclei, and with a sufficient number of kink sites at its edge to accept any incoming adatom. This allows one to consider only a one-dimensional case for surface diffusion. An atom approaching a step of height h normal to the surface either diffuses and incorporates at the step edge, adsorbs and forms a nucleus on the terrace, or desorbs. Figure 2 depicts the resulting fluxes, where J_s , J , n_s , τ_s , and λ_0 are the surface diffusion flux, adatom arrival flux from the gas phase to the surface, adatom density on the surface, mean residence time, and terrace width, respectively.

Using Einstein's relation, the surface diffusion length, λ_s , is directly related to the diffusion coefficient on the surface, D_s , and τ_s . It can also be expressed in terms of the diffusion barrier energy, E_d , and the energetic barrier to be surmounted for desorption, which is the same as the adsorption energy, E_{ad} .²⁵

$$\lambda_s = \sqrt{D_s \tau_s} = \lambda_e e^{\frac{E_{ad}-E_d}{2k_B T}}. \quad (1)$$

Here, λ_e is the effective elementary jump distance on the surface or the distance between two neighboring lattice sites.

In absence of nucleation, the net flux adsorbing at the surface, $J_v(x)$, must be equal to the diffusion flux toward the steps. Therefore, if the steps are assumed to be perfect sinks, i.e. the capture probability at the steps is unity, then the following continuity equation describes the system:

$$\frac{\partial J_s(x)}{\partial x} = J - \frac{n_s(x)}{\tau_s} = J_v(x), \quad (2)$$

where the right hand side of the equation represents the net flux arriving at the surface.

Since the diffusion flux is proportional to the change in adatom concentration, J_s must be directly proportional, through D_s , to the gradient of n_s . Considering this, the adatom density as a function of the position on the terrace can be arrived upon:

$$n_s(x) = J\tau_s + (n_{s0} - J\tau_s) \frac{\cosh\left(\frac{x}{\lambda_s}\right)}{\cosh\left(\frac{\lambda_0}{2\lambda_s}\right)}, \quad (3)$$

where the step is used as a boundary condition and $x=0$ is at the middle of the terrace (see Figure 2). It is assumed that the step is at equilibrium and has an adatom density of n_{s0} . Since the surface supersaturation, σ_s , is given as the relative difference between n_s and n_{s0} , Equation 3 can be used to derive the surface supersaturation as a function of the position on the surface as:

$$\sigma_s(x) = \frac{n_s(x) - n_{s0}}{n_{s0}} = \left(\frac{J\tau_s}{n_{s0}} - 1\right) \left(1 - \frac{\cosh\left(\frac{x}{\lambda_s}\right)}{\cosh\left(\frac{\lambda_0}{2\lambda_s}\right)}\right). \quad (4)$$

Through the original BCF treatment, σ_s is directly related to the vapor supersaturation, σ , which for AlN growth from the vapor phase, like MOCVD, is given by the relative difference between the input partial pressure of the Al, p_{Al}^0 , and the equilibrium vapor pressure of Al, p_{Al} :

$$\sigma = \frac{p_{Al}^0 - p_{Al}}{p_{Al}}. \quad (5)$$

The vapor supersaturation describes the deviation of the growth system from the thermal equilibrium and represents the driving force for the growth. Considering the BCF relationship, the net adatom arrival flux (Equation 2) as a function of the position on the surface can be rewritten as:

$$J_v(x) = \frac{n_{s0}}{\tau_s} (\sigma - \sigma_s(x)). \quad (6)$$

Therefore, using this relationship and Equations 2 and 4, one can express σ_s in terms of σ as:

$$\sigma_s(x) = \sigma \left(1 - \frac{\cosh\left(\frac{x}{\lambda_s}\right)}{\cosh\left(\frac{\lambda_0}{2\lambda_s}\right)} \right). \quad (7)$$

Equation 7 indicates a direct relationship between the vapor supersaturation and surface kinetics and allows for a better understanding of the relation between the input growth parameters and the kinetics of the adatoms on the surface. It indicates that σ_s reaches a maximum at the center of the terrace. It is important to note that this kinetic theory treatment results in a symmetric n_s due to the assumed symmetric boundary conditions. As can be seen from Figure 1 (b), which shows nucleation on the middle of the terraces rather at the down-steps, the Ehrlich-Schwöbel barrier is negligible within our growth parameter space. However, even if slightly

asymmetric boundary conditions exist due to the fact that the probabilities for uphill and downhill adatom diffusion occurring at a step edge might be different, the assumption of symmetrical boundary conditions does not take away from the overall trends that will be discussed and supported through the experimental results.

The first observation that this model can explain is the formation of nuclei on the terraces. If the maximum of the surface supersaturation profile across a step exceeds a critical surface supersaturation value, σ_s^* , then nucleation will occur with high probability. The maximum of Equation 7 is reached at $x=0$ and gives the maximum surface supersaturation as:

$$\sigma_{s,max} = \sigma \left(1 - \frac{1}{\cosh\left(\frac{\lambda_0}{2\lambda_s}\right)} \right). \quad (8)$$

To use simply the input partial pressure of precursors and thermodynamics to determine σ would result in a maximum value representative of an ideal case where no pre-reactions or other transport losses take place. To more accurately capture the effective σ near the surface, a value obtained from the growth rate, R , must be considered, since R can be measured accurately and it directly determines the adatom incorporation at the step edge. The growth rate is given by the product of the step velocity, v , and the h/λ_0 ratio. The step velocity can be expressed as:

$$v = 2 \frac{J_s\left(\frac{\lambda_0}{2}\right)}{n_0}, \quad (9)$$

wherein adatoms diffusing from both directions toward the step have been taken into account. Here, n_0 is the density of adatom sites on the surface. By accounting for R , $\sigma_{s,max}$ can be reformulated using Equations 2, 6, 8, and 9 to the following form:.

$$\sigma_{s,max} = \frac{R\tau_s\lambda_0n_0}{2h\lambda_sn_{s0}} \tanh\left(\frac{\lambda_0}{4\lambda_s}\right). \quad (10)$$

In Equation 10, R , λ_0 , λ_s , and h can be determined experimentally. Also n_0 is a known intrinsic material parameter. However, the residence time, τ_s , and adatom density at the steps, n_{s0} , must be determined in some other manner. Even though it is difficult to separately quantify n_{s0} and τ_s , the ratio between the two can be determined through the Hertz-Knudsen equation,²⁶ which can be expressed for AlN growth as:

$$\frac{n_{s0}}{\tau_s} = \frac{P_{Al}}{\sqrt{2\pi m_{Al} k_B T}}, \quad (11)$$

where m_{Al} is the mass of an Al adatom. For the case of the AlN step flow growth, only the metal species have to be considered under typical growth conditions since the V/III ratio is much greater than unity and the growth rate is limited by the supply of metal atoms.

The equilibrium vapor pressure can be calculated by considering the chemical reaction that takes place during growth:¹³

The metalorganic source is not included in this reaction because the thermolysis of the TMA into the Al gas phase is highly spontaneous. The corresponding equilibrium equation is:

$$K_{Al} = \frac{a_{AlN} P_{H_2}^{3/2}}{P_{Al} P_{NH_3}}, \quad (13)$$

where a_{AlN} , p_{H_2} , and p_{NH_3} are the activity of AlN, partial pressure of H_2 , and partial pressure of NH_3 , respectively, and $\log_{10} K_{AlN} = -14.2 + (3.17 \times 10^4)/T + 2.33 \log_{10} T$.²⁷ By using the methodology previously described by Mita et al.,²³ a fourth order polynomial equation can be derived for determining the equilibrium vapor pressure, p_{Al} :

$$P_{Al}^4 + \left[2C_1 + 8 \frac{a_{AlN}^2}{K_{AlN}^2} \right] P_{Al}^3 + \left[C_1^2 - 12 \frac{a_{AlN}^2}{K_{AlN}^2} C_2 \right] P_{Al}^2 + 6 \frac{a_{AlN}^2}{K_{AlN}^2} C_2^2 P_{Al} - \frac{a_{AlN}^2}{K_{AlN}^2} C_2^3 = 0 , \quad (14)$$

where $C_1 = p_{NH_3}^0 - p_{Al}^0$, $C_2 = p_T + p_{Al}^0 - p_{NH_3}^0$, and $p_{NH_3}^0$ and p_T are the input partial pressure of NH_3 and total pressure, respectively.²³

Classical nucleation theory gives that the critical nucleation rate, R_{2D}^* , is proportional to the rate at which the molecules attach to the supercritical nucleus, j^* , the probability of a nucleus overcoming the critical energetic barrier (Zeldovich nonequilibrium factor), Z , and the equilibrium concentration of critical nuclei, N^* . This can be approximated for AlN as:

$$R_{2D}^* = j^* Z N^* \approx e^{65 - \frac{\Delta G_{2D}^*}{k_B T}} , \quad (15)$$

where ΔG_{2D}^* is the critical free energy of 2D nucleation, which is directly related to the change in the chemical potential of the process,²⁸ which can be expressed in terms of σ_s . The resulting relationship for ΔG_{2D}^* is then given by

$$\Delta G_{2D}^* = \frac{\pi h^2 A \gamma_s^2}{k_B T \ln(\sigma_s^* + 1)} \quad (16)$$

where γ_s and A are the surface free energy at the step and the projected area of an adatom, respectively. Substituting Equation 16 into Equation 15 gives the critical surface supersaturation where the onset of nucleation should be favored:

$$\sigma_s^* = e^{\frac{\pi h^2 A \gamma_s^2}{k_B^2 T^2 [65 - \ln(R_{2D}^*)]}} . \quad (17)$$

The transition between the step-flow growth and 2D nucleation and 3D growth can be observed experimentally, as shown in Figure 1. By setting Equations 10 and 17 equal to each other, surface diffusion parameters at growth conditions can be obtained by determining the

transition point experimentally. Furthermore, it is evident from these arguments that supersaturation, as well as the misorientation angle of the substrate, i.e. the terrace width, control the steady state surface morphology during growth.

B. AlN Homoepitaxial Growth

To better understand the surface kinetics of AlN homoepitaxial growth and to ultimately have the ability to control the type of surface morphology grown, the model described in the previous section was applied to the AlN homoepitaxial films. In order to apply the model, λ_s should be quantifiable, however, this is not straightforward due to the fact that γ_s is unknown; it has not been experimentally determined for any III-nitride to our knowledge. Therefore, an experimental method for determining λ_s is considered and used to indirectly arrive at γ_s . Figure 3 shows a surface where the terraces are wide enough, for given supersaturation, to support formation of 2D nuclei. The mean distance between the observed nuclei should be approximately twice λ_s . Using this approach, 1 μm -thick AlN homoepitaxial films were deposited on a range of misoriented substrates with a growth rate and temperature of 500 nm/hr and 1250°C, respectively, in order to determine the critical point for 2D nucleation. From these results, the surface diffusion length was determined to be 46 ± 13 nm. This value is reasonable since the denuded zone at the step was measured to be 60 to 110 nm.

With the diffusion length known, the surface energy was calculated to be 149 ± 8 meV/Å² from Equations 10, 11, and 17. The surface energy changes very slowly with a large deviation in λ_s due to the exponential in Equation 17, helping to validate the use of the calculated γ_s value. According to these results, the surface energy of the Al-polar surface of AlN is of the same order of magnitude as that of the (1-100) and (11-20) planes, which were predicted from density functional theory by Jindal et al. to be 175 and 187 meV/Å², respectively.²⁹ Furthermore,

this result can be used to corroborate current theoretical models that try to predict the surface energy. Additionally, it is interesting to note that this γ_s value is close to 139 meV/Å², the γ_s value reported for (111) 3C-SiC (Si face), which has the same atomic configuration near the surface as (0001) 6H-SiC (Si face).⁹

With γ_s , the derived model from Section A can be used in a quantitative and predictive manner. Equation 8 indicates that the critical point between 2D nucleation and the step flow growth mode will directly depend on σ . Figure 4 shows the theoretical curves for σ , applying the same thermodynamic methodology as reported by Mita et al.,²³ but now for AlN growth as a function of the growth rate for $T = 1050, 1150, \text{ and } 1250^\circ\text{C}$, and as a function of growth temperature for $R = 500, 1000, \text{ and } 2000 \text{ nm/hr}$. These growth conditions were chosen to represent typical range of supersaturations achievable by most MOCVD systems. Since the vapor supersaturation increases with an increase in the growth rate and decreases with growth temperature, one should observe 2D nucleation both at large growth rates or low temperatures.

To demonstrate the dependence of the critical point on growth rate, Figure 5 shows the surfaces of AlN films grown at two different growth rates. The misorientation angle and growth temperature were kept constant at 0.3° and 1150°C , respectively. A growth rate of 2000 nm/hr resulted in 3D nuclei, similar to those shown in Figure 1 (a). The islands are slightly tilted in Figure 5 due to a higher misorientation angle as compared to the surface shown in Figure 1 (a). With a reduction in the growth rate to 500 nm/hr, the growth transitioned to a purely step flow growth mode, resulting in atomically smooth bilayer step morphology. This observation is consistent with the above discussion, since a reduction in R requires that $\sigma_{s,max}$ is reduced, making nucleation on the terraces less likely. In other words, by sufficiently reducing the growth

rate, the maximum surface supersaturation was lowered to a value below the critical surface supersaturation.

Figure 6 demonstrates another way of transitioning from the 3D to step flow growth mode. The AlN homoepitaxial films shown in Figure 6 had a fixed misorientation angle and growth rate of 0.08° and 1000 nm/hr, respectively. Increasing the growth temperature from 1100°C to 1250°C , increased the surface diffusion length of the Al adatoms, reducing the maximum surface supersaturation. These results indicate that with the increase in the growth temperature, $\sigma_{s,max}$ was reduced below the σ_s^* . As predicted from the model, the critical points found through adjusting the growth rate and growth temperature both correlate with about the same σ , as can be seen in Figure 4. Furthermore, after taking into account the misorientation angle and diffusion length, the $\sigma_{s,max} = \sigma_s^*$ values were identical to one another and both values matched the measured σ that was used to calculate the surface energy. These results seem to be self-consistent and indicate the predictive nature of the proposed model. Moreover, this indicates that other parameters that directly affect σ , such as the V/III ratio, diluent gas, and total pressure during growth, could also be considered to arrive at the same result. An important conclusion from these results is that by understanding the surface kinetics, one can select the desired growth mode by appropriately changing the vapor supersaturation through adjusting one or more of the growth parameters.

The effect of the substrate misorientation angle, α , was also investigated by keeping the homoepitaxial AlN growth conditions constant with a growth rate of 500 nm/hr and temperature of 1250°C . The intentional substrate misorientation was shown to modify the step morphology from bilayers to step-bunches with increasing α . By growing AlN on vicinal (0001) substrates misoriented from 0 to 4° , the critical misorientation angle, α^* , for the transition from the bilayer

steps to step-bunches, for the parameter space given above, was determined to be $\sim 0.25^\circ$. Figure 7 demonstrates this transition, where an abrupt increase in step height represents the onset of step-bunching. For quantification of the step-bunched morphology, the step height and terrace width were taken from the entire macro-step, even though bilayer steps were present on the terraces, as shown in Figure 1. Below a critical misorientation angle, in this case 0.25° , the step height was consistently measured to be $2.5 \pm 0.1 \text{ \AA}$ and the terrace width deviated as $\lambda_0 = h/\tan(\alpha)$ with the misorientation angle. The macro-step height increased with an increase in α , however, the terrace width remained relatively constant in the misorientation range from 0.25 to 0.62° . A film grown with 4° misorientation (not shown in Figure 7) resulted in a macro-step height and terrace width of 14 nm and 300 nm , respectively. This observation indicated that the terrace width began to decrease beyond a certain misorientation angle. All of these general trends were found to be independent of the misorientation direction. The only differences observed for misorientations toward $[1-100]$ as compared to $[11-20]$ was the step edge shape, as discussed earlier and depicted in Figure 1.

A similar study was also carried out on AlN films grown on AlN templates on sapphire. For a constant growth rate of 500 nm/hr and temperature of 1250°C , it was found that the critical misorientation angle was independent of the type of the substrate used. Interestingly, α^* for the given growth conditions was determined to be around 0.25° as well. Even though the film growth was initiated through 3D nucleation on the hetero-interface and continued by the coalescence of these nuclei, once the film was coalesced and spiral step flow growth established, the absolute step density of the substrate still had an effect on the type of surface morphology that developed. This suggested that the transition from the bilayer stepped to step-bunched morphology for a given initial step density was solely dependent on the adatom surface kinetics

during growth. More importantly, the strain state of the heteroepitaxial AlN films was significantly different from that of the homoepitaxial AlN films. In particular, the heteroepitaxial films were in tension whereas the homoepitaxial films were strain-free, as determined by HRXRD studies. Bilayer steps and step-bunches were present on strain-free homoepitaxial films and heteroepitaxial films with the same strain state indicating that these morphology types were independent of the strain state of the film. These results indicated that the surface morphology transition was likely not initiated by strain as suggested by Tersoff et al.³⁰ The bilayer step fronts were always uniformly parallel and straight for AlN growth on AlN because of the low dislocation density ($<10^3 \text{ cm}^{-2}$); however, with higher dislocation densities in the AlN heteroepitaxial films on sapphire, step pinning occurred by the dislocations intersecting the surface. Figure 8 shows this step pinning through representative AFM images of the surface of a bilayer stepped and step-bunched morphology for AlN films grown on AlN templates on sapphire. This step pinning roughened the surface, however, it did not affect α^* .

If the transition between the bilayer and macro steps depends solely on surface kinetics, one should be able to invoke it by controlling the diffusion length of adatoms by changing the surface supersaturation by changing one of the input parameters (temperature, V/III ratio, carrier gas, pressure ...). To verify this point, AlN films with a growth rate of 500 nm/hr were grown on AlN substrates with a fixed α of 0.35°. At a growth temperature of 1250°C, step-bunching occurred, as shown in Figure 9 (left). Following the framework discussed above, in order to transition from step bunching to step flow, one would need to increase surface supersaturation, which can be accomplished by lowering the growth temperature. Indeed, by lowering the growth temperature to 1100°C, a transition from macro-step to bilayer step morphology was observed (Figure 9 (right)), corresponding to a shift in α^* with growth temperature. Further studies

experimental showed that decreasing or increasing the growth temperature consistently resulted in an increase or decrease in α^* , respectively. It was found that if the surface diffusion length of Al adatoms was smaller or comparable to the terrace width, a bilayer step morphology was obtained; if the diffusion length was longer than the terrace width, a step-bunched morphology was obtained. It is important to note that this trend was also found to be independent of the substrate upon which the AlN layer was grown, further supporting the finding that the step-bunching phenomena is solely dependent on the adatom surface kinetics.

The exact reason for the onset of step-bunching is still under debate. Usually, it is attributed to the surface kinetics of adatoms through the Schwoebel effect, however, others have suggested the cause to be related to short range attractions between steps, and some from partial relaxation of a strained vicinal layer.³⁰⁻³² The results in this study suggest that step-bunching is not a response to strain. Rather, this phenomenon seems to be a result of an instability in the step advancement rate from step to step due to the attachment probability differences. This instability will result in some terraces shrinking and others expanding, resulting in step-bunching. Regardless of the exact formation mechanism, the important outcome of this study is that step-bunching can be controlled and even reversed by adjusting the diffusion length of adatoms via control of the supersaturation of the growth species.

C. Implications for Other Surfaces

In addition to explaining and predicting the growth mode on the Al-polar surfaces, these results provide a predictive framework for determining growth conditions that would be needed to achieve the desired growth modes on N-polar, semi-polar, and non-polar AlN surfaces via corresponding surface energies. These surface energies have not yet been determined experimentally and will be different from γ_s of the Al-polar surface determined in this work. For

example, the surface energies of the (0001) 6H-SiC (Si face) and (000-1) 6H-SiC (C face) have been reported to be 139 and 19 meV/Å², respectively, indicating nearly an order of magnitude difference.⁹ Accurately calculating the surface energies for different surfaces from the first principles is quite challenging since this requires a precise depiction of the surface reconstruction during growth. Since surface reconstruction depends on the thermodynamics, growing under N-rich as opposed to III-rich conditions will result in different surface reconstructions.³³ In particular, the role of hydrogen in the surface reconstruction of polar AlN is thought to be significant through thermodynamic considerations, yet this has not been verified experimentally.³⁴ For these reasons, only the implications for surface energies different than 149 meV/Å², which serve to represent N-polar, semi-polar, and non-polar surfaces, should be considered.

Based on the developed model, the transition from the 3D nucleation and to step flow growth mode directly depends on σ_s^* . For surfaces with γ_s lower than 149 meV/Å², σ_s^* would be smaller than it is for the Al-polar AlN, meaning that using the same growth conditions as were used for the Al-polar AlN growth would result in a higher probability of 3D nucleation. In order to maintain the same growth mode, such a surface would require a lower vapor supersaturation during growth to achieve atomically smooth surfaces by the step flow growth mode. This could be realized by growing at higher temperatures or with lower growth rates, following the process parameters used in this work. In addition to using a lower vapor supersaturation, the substrate misorientation could be increased to reduce $\sigma_{s,max}$ below the value of σ_s^* . This technique has been used for achieving smooth N-polar GaN epitaxial film surfaces.³⁵ Other parameters, such as diluent gas, total pressure, and V/III ratio could also be considered for reducing the vapor supersaturation as discussed by Mita et al. and Rice et al.^{13, 23, 36} As an example, a decrease in γ_s

of one order of magnitude would require a subsequent decrease in σ_s^* of over three orders of magnitude. Figure 4 suggests the growth condition changes that would be required to achieve atomically smooth surfaces in such a case. Conversely, with γ_s greater than $149 \text{ meV}/\text{\AA}^2$, the step flow growth mode would be easier to achieve for the growth conditions that otherwise favor 3D growth on the Al-polar AlN. In such a case, a significant increase in the vapor supersaturation would be necessary to transition into the 3D growth mode.

Figure 10 gives a schematic summary of all the trends that were observed in AlN films and are predicted from the model. This schematic illustrates the direction of change of the vapor supersaturation or/and misorientation angle to transition to the desired growth mode. It is important to emphasize that in addition to temperature, the vapor supersaturation can be modified by many other controllable growth parameters, such as V/III ratio, diluent gas, or total pressure. While these growth parameters were not a direct subject of this study, they can be understood through the same model. For a given surface misorientation, 3D islands can be avoided by reducing the vapor supersaturation whereas removing step-bunches requires a reduction in the surface diffusion length, which is achieved by increasing the supersaturation. It is important to note that the developed scheme is not specific to AlN. These concepts are universally applicable to control any epitaxial growth on any substrate. By controlling the supersaturation in the vapor phase, the surface kinetics can be modified to yield any type of desired surface as long as the necessary conditions can be achieved within the parameter space of a specific deposition system.

IV. Conclusions

A surface kinetic framework for control of surface morphology during AlN growth on Al-polar surfaces by MOCVD has been developed. Films grown with both high and low

dislocation densities were investigated, indicating the importance of realizing low dislocation densities to achieve the desired long-range step-flow growth and flat surfaces. Step morphology dependence on substrate misorientation and vapor supersaturation, as demonstrated by changing the growth rate and growth temperature, were observed and explained. BCF theory was utilized to understand these dependencies. The surface energy, a critical parameter controlling surface kinetics during growth, of the Al-polar surface of AlN was experimentally determined to be $149 \pm 8 \text{ meV}/\text{\AA}^2$ using the proposed model. The onset of different growth modes was found to depend on the surface diffusion length with respect to the terrace width. The same surface morphology could be achieved either by changing the misorientation angle, which controlled the terrace width, or vapor supersaturation, which controlled the surface diffusion length. For a fixed vapor supersaturation, a critical misorientation angle existed for the transition between bilayer steps and step-bunches, however, this critical misorientation angle could be controlled by the vapor supersaturation to some degree. This work offers a deeper understanding and a practical framework for control of surface morphology in Al-polar AlN epitaxy that is applicable to other AlN surfaces and even other materials by applying the appropriate surface energy.

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Figure 1: AFM images representing the 6 distinct types of surface morphologies attainable for AlN epitaxial layers grown with the absence of dislocations. The distinct features include 3D island formation (a), bilayer steps with (b) and without (c) 2D nuclei, and different types of step bunching (d)-(f).

Figure 2: Schematic of an ideal step and terrace morphology and the motion of species (adapted from Ref. 8).

Figure 3: AFM image of a bilayer stepped surface with 2D nuclei on the terraces.

Figure 4: Al vapor supersaturation as a function of growth rate (red) for $T = 1050^\circ\text{C}$ (dotted), 1150°C (dashed), and 1250°C (solid). Also plotted is the Al vapor supersaturation as a function of growth temperature (black) for $R = 500$ nm/hr (dotted), 1000 nm/hr (dashed), and 2000 nm/hr (solid).

Figure 5: AFM images representing AlN homoepitaxial films grown at different growth rates but a fixed misorientation angle and growth temperature of 0.3° and 1150°C , respectively.

Figure 6: AFM images representing AlN homoepitaxial films grown at two different temperatures but a fixed misorientation angle and growth rate of 0.08° and 1000 nm/hr , respectively.

Figure 7: Step height and width as a function of misorientation angle for AlN homoepitaxial films grown with a growth rate and temperature of 500 nm/hr and 1250°C, respectively.

Figure 8: Representative AFM images of AlN heteroepitaxial films deposited on sapphire with misorientation angles below (left) and above α^* (right).

Figure 9: AFM images representing AlN homoepitaxial films grown with a fixed growth rate of 500 nm/hr and α of 0.35° at two different temperatures showing macro-steps (left) and bilayer steps (right).

Figure 10: Schematic representing different growth morphologies and the direction of parameter changes required to transition from one morphology to the other.