Initial stages of GaN/GaAs(100) growth by metalorganic chemical vapor deposition

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A study of GaN buffers grown by metalorganic chemical vapor deposition on (001) GaAs substrates was performed. Nucleation images obtained by atomic force microscopy (AFM) were employed to investigate the growth temperature, growth time, and growth rate dependence of the nucleation mechanisms. The growth mode corresponds to two-dimensional (2D) island nucleation at low temperatures, while three-dimensional (3D) island growth is observed at high temperatures. Large grain sizes and good surface coverage was obtained for 3 min growth. Higher growth rates help nucleation on mismatched substrate and promote the 2D growth mode. GaN films 0.5 μm thick were grown on different buffers using a two-step technique as suggested by the AFM analysis and their morphology was found to improve when grown on optimized buffers. © *1996 American Institute of Physics.* [S0021-8979(96)01815-4]

I. INTRODUCTION

Optoelectronic components from blue to ultraviolet wavelengths, as well as, high-power and high-temperature devices can benefit from recent developments of GaN materials.[1,2] Progress on the use of GaN for device applications has, however, been slowed by the presence of large lattice mismatch for growth on commonly used substrates such as sapphire as well as other alternatives, i.e., GaAs and SiC. Buffer layers between the substrate and the nitride layer have been explored as a possible way to overcome these difficulties and resulted in improved material quality, as already demonstrated by various experimental results.[3–5] Improved quality epitaxially grown GaN films require, however, a good understanding of the growth parameters and mechanisms involved in buffer growth.[6–8] A first analysis along these lines has been presented by the authors based on theoretical growth modeling considerations[9] and experimental studies based on atomic force microscopy (AFM).[10] This article provides further insight into the underlying mechanisms of buffer growth by consideration of the growth mechanisms, and AFM analysis of GaN nucleation layers under various growth conditions. Section II describes the various growth modes present in heteroepitaxial processes as, for example, applied to the case of GaN growth on GaAs. The metalorganic chemical vapor deposition (MOCVD) process employed for growing the GaN layers investigated in this work and the techniques used for their AFM characterization are described in Sec. III. Section IV presents the experimental results obtained by this technique under various growth conditions. The quality of films grown on different buffers is also evaluated in Sec. V.

II. HETEROEPITAXY CONSIDERATIONS AND RELATED GROWTH MODES

There are various factors influencing epitaxial growth and the quality of the resulting films. These include parameters such as the rates of impingement of species, growth temperature, surface migration rates of reactants, the bond strengths and bond lengths of the substrate and overgrowth atoms, and the nucleation processes. Depending on the importance of these parameters, heteroepitaxial growth can take place under different modes which may be classified under three main categories: Frank–van der Merwe (FvdM) or layer-by-layer two-dimensional (2D) growth, Volmer–Weber (VW) or three-dimensional (3D) island growth, and Stranski–Krastanow (SK) or layer-by-layer plus island growth, as shown in Fig. 1.[11] The growth mode characteristic of a particular material system under equilibrium conditions is found to depend on the cluster-vapor interfacial free-energy $\sigma_{\text{C-V}}$, the substrate-vapor interfacial free-energy $\sigma_{\text{S-V}}$, the cluster-substrate interfacial free-energy $\sigma_{\text{C-S}}$, and the strain energy σ_{st} due to lattice mismatch. A schematic of these energy terms and the contact angle definition of a GaN cluster is shown in Fig. 2. When the substrate surface energy exceeds the sum of the surface energy of the epilayer (cluster) and the interfacial cluster-substrate energy (i.e., $\sigma_{\text{s-v}}>\sigma_{\text{c-v}}+\sigma_{\text{c-s}}$), the film grows in the FvdM mode. If this condition is not met, the VW mode will pertain. A more detailed analysis reveals that the accumulated strain energy σ_{st}, which increases as the growth of the epilayer progresses, should also be considered in determining the growth mode. In fact, although the condition $\sigma_{\text{s-v}}>\sigma_{\text{c-v}}+\sigma_{\text{c-s}}$ may be satisfied in a growth system, the strain energy σ_{st} can reverse the inequality in the complete formula $\sigma_{\text{s-v}}>\sigma_{\text{c-v}}+\sigma_{\text{c-s}}+\sigma_{\text{st}}$ resulting in a change from 2D to 3D growth. This situation corresponds to the SK growth mode.

The above discussed growth modes will determine the formation of the nucleation layers for GaN growth. The initial stages of growth and the resulting nucleation layers strongly influence the type and quality of the final layer. It is therefore very important to study the nucleation layer formation under different conditions of growth. Nucleation and growth involves atoms in the vapor phase condensing on the substrate, and then forming clusters of adatoms. As already mentioned, the formation of the clusters is controlled by the

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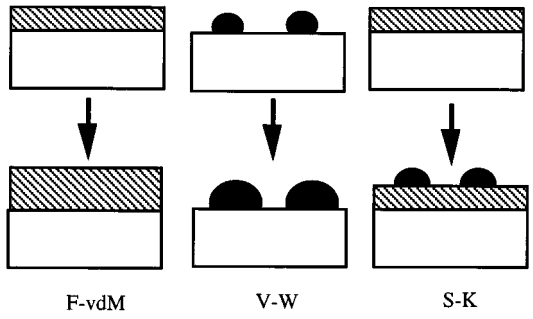

FIG. 1. Schematic of the three possible growth modes: Frank–van der Merwe, Volmer–Weber, and Stranski–Krastinov.

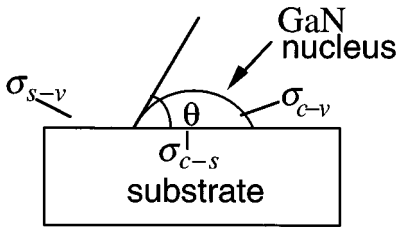

FIG. 2. An illustration of the energy terms and contact angle definition of a GaN cluster on a foreign substrate.

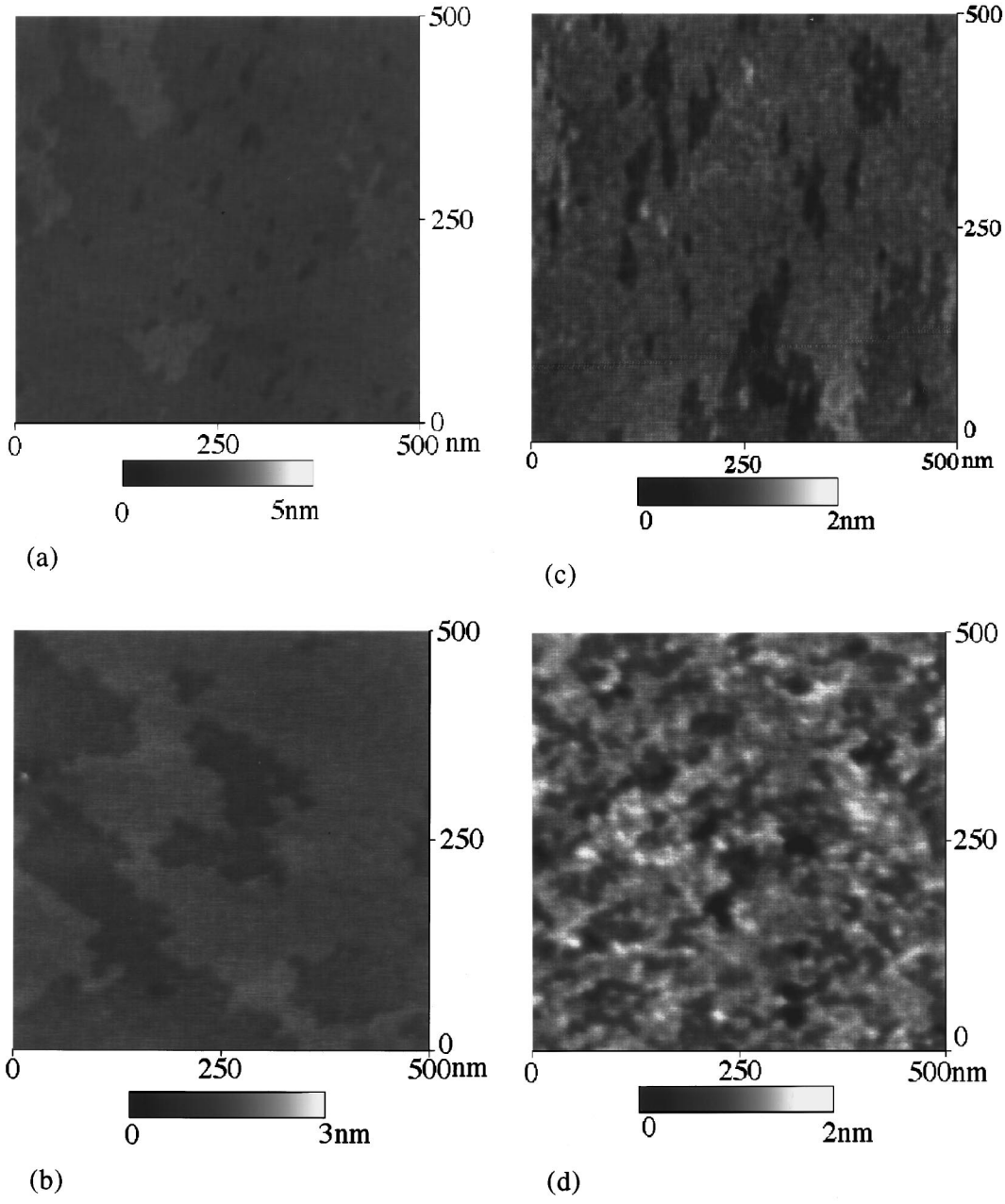

FIG. 3. AFM images of GaN nucleation layers grown on (001) GaAs for 1 min at a temperature of (a) 450, (b) 500, (c) 550, and (d) 600 °C.

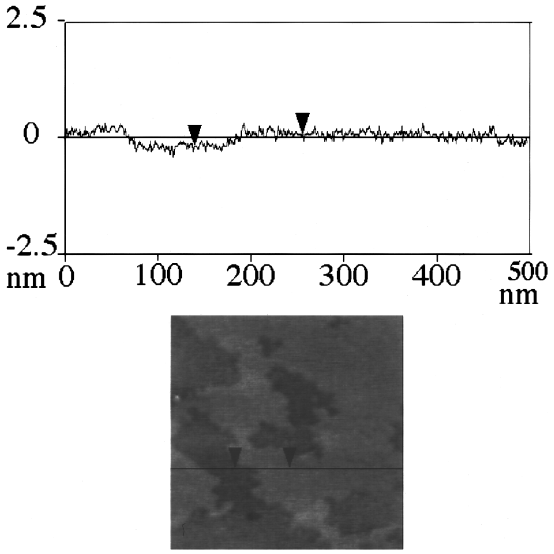

FIG. 4. The AFM extracted cross section of GaN nucleation layer grown at 500 °C for 1 min.

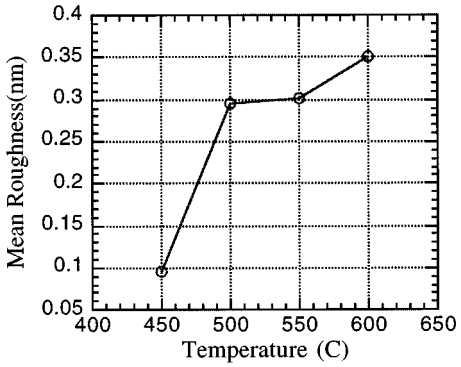

FIG. 5. The AFM extracted roughness of GaN nucleation layers grown for 1 min vs growth temperature.

energy terms of the system under study. The inherent properties of GaN should play a crucial role in determining the energy balance conditions in GaN growth. To evaluate the latter one needs to consider the bonding strength between Ga–N and Ga–As in conjunction with the atomic arrangements at the initial growth stage.

Due to its wide band gap, GaN should display a very strong bonding strength compared with GaAs. This can be understood by the next considerations. The lattice constant of GaAs and GaN is 5.65 and 4.5 Å, respectively, and the associated atomization energies are 155.5 and 205.6 kpm.[12] One may also expect that GaN has a shorter bond length and larger bond energy than GaAs. Let us next consider the fact that the surface of the GaAs substrate is As stabilized under normal growth conditions. This implies bonding of Ga–As first, followed by Ga–N bonding. As a result, the energy between the substrate and deposit is determined by Ga–As bonding and is therefore expected to be smaller than the energy between the deposit and the vapor which is related to Ga–N bonding. This situation can be described as determined by the condition $\sigma_{C\text{-}V} > \sigma_{S\text{-}V} - \sigma_{C\text{-}S}$. In this case, the contact angle

$$\cos\,\theta = \frac{\sigma_{S\text{-}V} - \sigma_{C\text{-}S}}{\sigma_{C\text{-}V}} \tag{1}$$

of the critical nuclei would be expected to be large.[13] As a result, nucleation of GaN on a foreign substrate would be difficult. Reduced lateral growth and promotion of VW (3D, island) growth may therefore take place. Under such circumstances, ''wetting'' of the substrate by the epitaxial layer is very little or equivalently speaking nucleation would be difficult.

In addition to the above considerations, nucleation is also governed by the growth temperature and the arrival rate of the reaction species. The nucleation rate can be increased by decreasing the growth temperature and by increasing the arrival rate of the reaction species.[14] Under such conditions, dense clusters would easily coalesce into larger 2D clusters and promote the lateral growth. However, the migration rate of the adatoms would decrease as the temperature decreases and low migration rates could lead to a rough nucleation layer surface. Another factor to be considered is the reduction of reactant decomposition rates as the temperature decreases in MOCVD growth. These factors set an additional limit to the minimum temperature that can be used for growth. Based on the preceding discussions it is clear that the growth temperature plays a key role in achieving nucleation layers of good morphology. Low growth temperatures could lead to increased N-sticking coefficients and therefore promotion of 2D growth by improving GaN adhesion. Although this seems to be favorable for GaN buffer growth, increased surface roughness and decreased reactant decomposition under such conditions may set a limit to the lowering of growth temperature. Optimum growth temperatures need consequently to be sought for buffer layer growth to balance the deposition and lateral migration. Complete substrate coverage and good buffer quality is crucial if buffer layers are to be used as templates for homoepitaxial growth of GaN. Substrate wetting also needs to be ensured for improved bulk GaN quality. The studies undertaken in this work attempt for this reason to provide an understanding of layer nucleation as a function of temperature and growth rate, and examine growth at various stages by examining samples grown over different times.

III. GROWTH OF GaN AND TECHNIQUES EMPLOYED FOR FILM CHARACTERIZATION

The GaN nucleation layers investigated in this study were grown on (001) GaAs by MOCVD. Their morphology was examined using AFM which is a powerful technique for surface topography analysis. Vertical layer thickness variations in the nanometer range can easily be detected by this technique making it an ideal tool for studying the formation of the initial nuclei and their subsequent growth and coalescence.

Low-pressure (60 Torr) MOCVD using H_2 carrier gas was used for growth and epi-ready GaAs substrates were

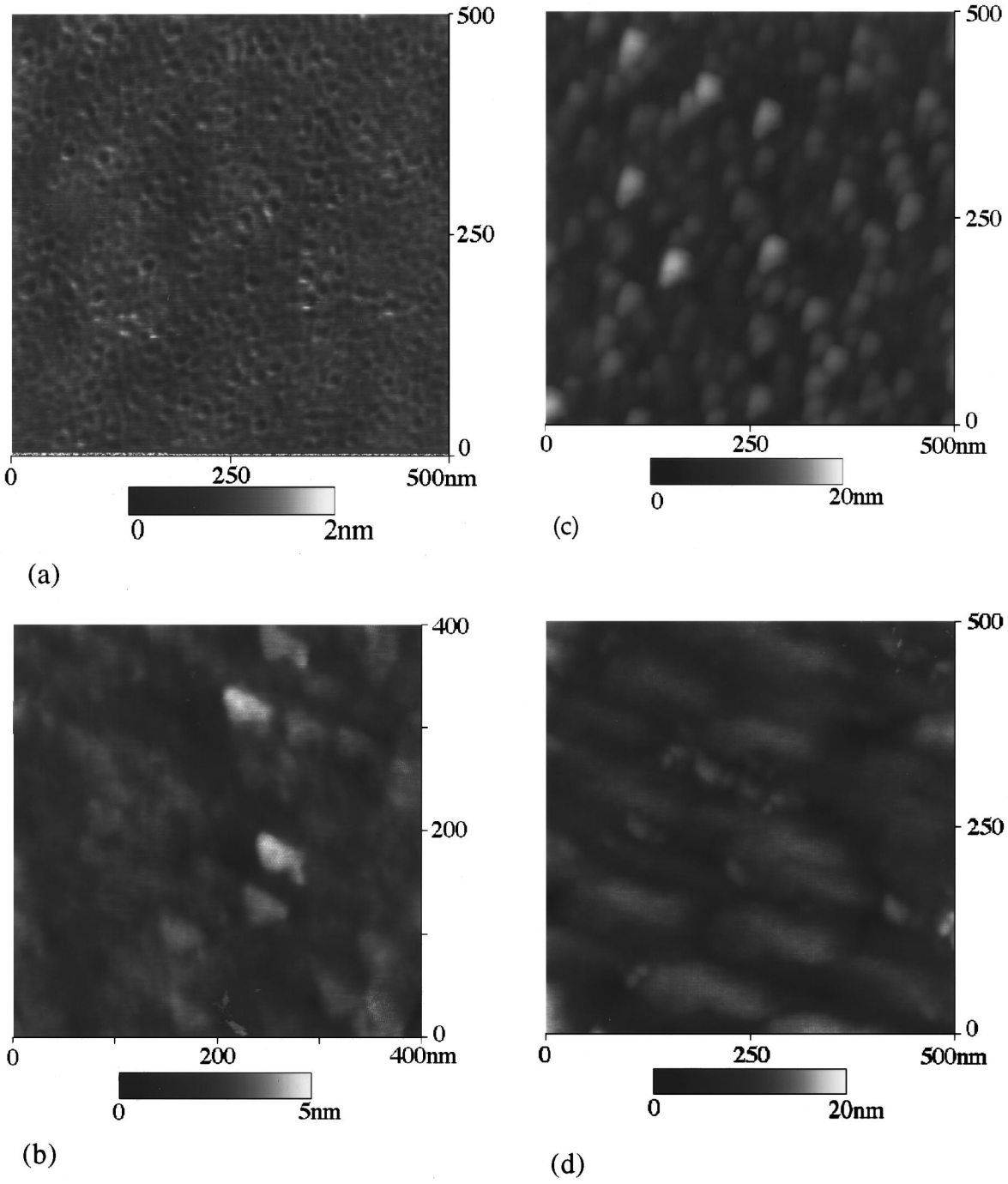

FIG. 6. AFM images of GaN nucleation layers grown on (001) GaAs at a temperature of 500 °C for (a) 2, (b) 3, (c) 6, and (d) 9 min.

employed. They were loaded in our in-house horizontal reactor and annealed in H_2 and AsH_3 at 670 °C for 5 min to remove the surface oxide. After cooling down to the desired growth temperature, NH_3 alone was supplied for 10 min so that surface nitridation could take place. Trimethylgallium (TMGa) and NH_3 were then supplied simultaneously and GaN films were grown. The TMGa flow rate was fixed at 13.4 μmol/min for all the experiments reported here except for the growth rate experiment reported later on in Sec. IV. The NH_3 flow was 1000 sccm. The H_2 supply rate was 2 slm. The samples were grown at a fixed V/III ratio of 3300 and substrate temperatures ranging from 450 to 600 °C. The growth rate of the buffer layer was determined by growing a thick nitride film using the same layer growth condition as for the buffer and examining its cross section using scanning electron microscopy.

The morphology of the nucleation layer was examined by using a Digital Instruments Nanoscope III AFM system with tapping mode. The structural properties of the subsequently grown GaN films were finally characterized by x-ray diffraction (XRD).

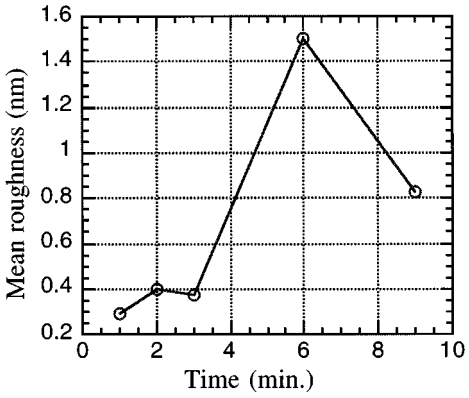

FIG. 7. The AFM extracted roughness of GaN nucleation layers grown at 500 °C vs growth time.

IV. AFM CHARACTERIZATION OF GaN NUCLEATION LAYERS

The impact of temperature on the buffer quality was examined first. GaN layers were grown for this purpose over a fixed time of 1 min and their growth temperature varied from 450 to 600 °C. A short growth time was employed in order to obtain layers of small thickness representative of buffer growth. The estimated thickness was of the order of 70 Å based on bulk growth thickness characteristics. AFM analysis of the layers was performed and the corresponding 2D plots are shown in Fig. 3. Figures 3(a)–3(d) depict the morphology of the nucleation layers as a function of the growth temperature [(a) 450, (b) 500, (c) 550, and (d) 600 °C.]

Small regions of 2D nucleation islands (~50 nm) could be observed in the case of 450 °C growth temperature. This suggests that the growth mode at low temperatures corresponds to two-dimensional (2D) nucleation. As the growth temperature increases to 500 °C, surface diffusion rates are apparently increased and the size of the 2D nucleation islands increases considerably (~300 nm). To confirm the presence of 2D sites in the nucleation layer, a cross-sectional view was obtained by AFM and is given in Fig. 4. The results indicate monolayer steps corresponding to 0.24 nm and confirm the 2D nucleation features of the layer.

Two-dimensional nucleation remained still the dominant mechanism when the temperature was further increased to 500 °C, but three-dimensional (3D) islands could also be observed. Three-dimensional island growth became finally the dominant mechanism at 600 °C and the surface roughness increased significantly. The film surface roughness is plotted in Fig. 5 as a function of growth temperature and indicates the surface roughness increase when the growth temperature is varied. Although the minimum roughness values indicated at 450 °C reflect the substrate rather than GaN morphology since substrate coverage is incomplete, one sees the need for relatively low growth temperatures in order to improve morphology. A growth temperature of 500 °C was selected for this purpose and used for the experiments discussed below.

As a next step in our buffer layer study we examined the influence of growth time for a constant growth temperature of 500 °C. Figure 6 shows the AFM images obtained in this

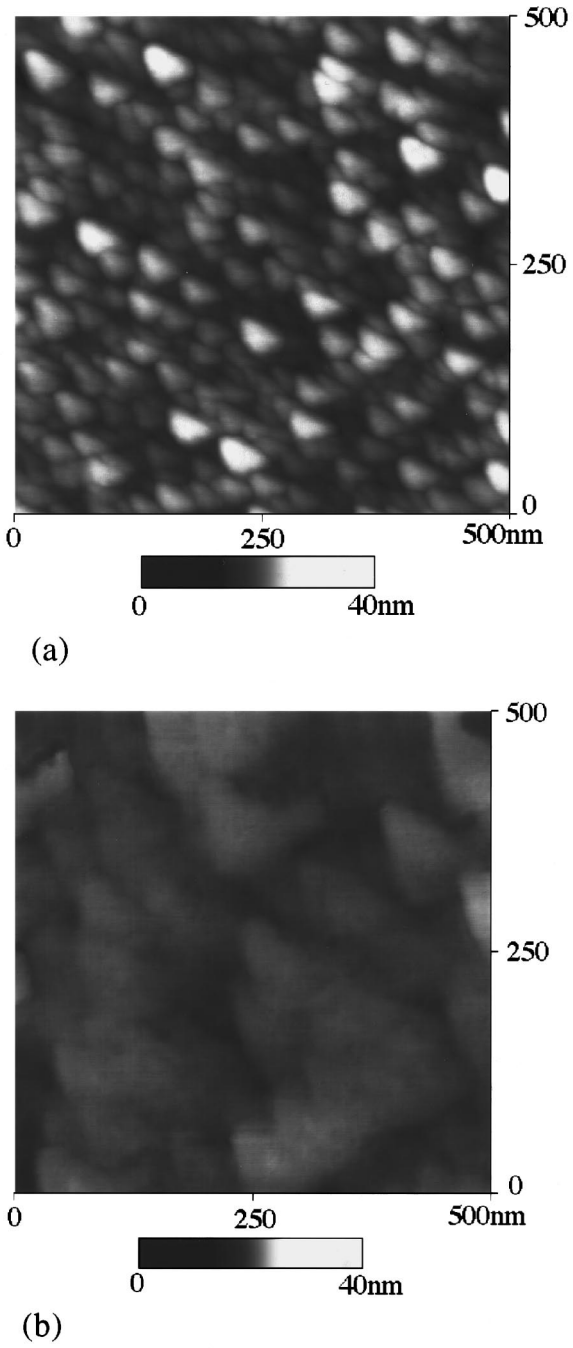

FIG. 8. AFM images of 200 Å GaN nucleation layers grown with a growth rate of (a) 27 and (b) 62 Å/min.

case for growth times varying from 2 to 9 min. Figure 7 shows the corresponding extracted surface roughness as a function of the growth time. The thickness of the film corresponding to this growth condition is around 200 Å as estimated based on growth of thick layers at the same temperature. The results of Figs. 5 and 6 indicate a comparable surface roughness for growth over 2 or 3 min. A 3 min growth time seems, however, to correspond to larger grain size and better surface coverage. Figures 6 and 7 also show that the roughness increases as the film becomes thicker and therefore buffer morphology degrades for growth times exceeding 3 min.

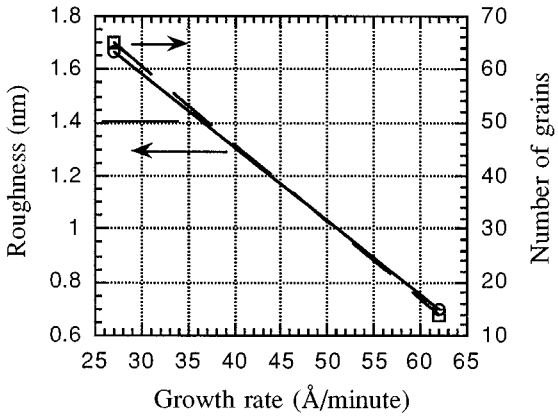

FIG. 9. The estimated roughness from AFM images vs growth rate.

The above observed trends of buffer morphology as a function of growth time may be explained by considering that once the substrate is completely covered with the nucleation layer, the subsequent GaN film is grown under homoepitaxial-like conditions. Thus the growth difficulties encountered at the initial growth stages are no longer faced and the deposited GaN film wets adequately the surface of the nucleation layer. The nucleation rate will in this case increase significantly. However, due to the relatively lower temperature used for buffer layer growth, the surface migration rates of the adatoms would be very small. Vertical growth would consequently take place faster than lateral growth and, as a result, the likelihood of layer-by-layer growth is reduced when the substrate is completely covered by the nucleation layer. There is consequently an optimum buffer layer growth time and growth should be divided into two steps: low growth temperature for the nucleation layer, and higher temperature for the ''bulk'' layer. Based on the above results it appears that a 3 min growth time corresponding to a ~200-Å-thick buffer is a good compromise since it results in minimum roughness combined with large grain size and good surface coverage.

To complete the study, the impact of growth rate on the morphology was also investigated. Here, the nucleation layer thickness was kept constant at 200 Å and the growth temperature was fixed at 500 °C, as indicated by the AFM studies. Separate experiments were carried out using thick layers in order to evaluate the appropriate conditions for variable growth rate from 27 to 62 Å/min. Figs. 8(a) and 8(b) show the AFM images corresponding to the nucleation layer morphology for a growth rate of 27 and 62 Å/min. The corresponding surface roughness and the number of the grains versus growth rate are shown in Fig. 9. The results of Figs. 8 and 9 indicate that as the growth rate increases the surface roughness and the number of grains is reduced. This could be understood by considering the nucleation mechanisms for GaN growth. Since the GaN nuclei have a large contact angle, adatoms will be difficult to ''nucleate'' on the substrate but easy to attach to an existing nucleus. When the incoming flux is low, the deposition will primarily concern ''growth'' of initial nuclei, which would lead to 3D growth. This mechanism can be conceptually considered as growth

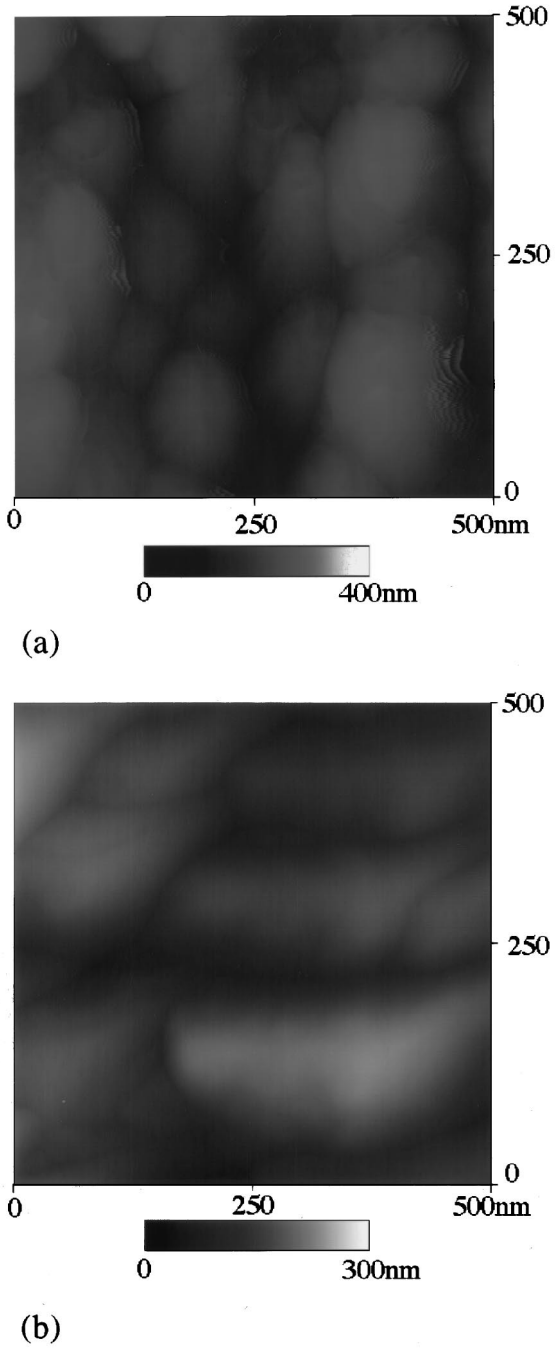

FIG. 10. AFM images of 0.5-μm-thick GaN layers grown on (a) buffer grown at $T=530$ °C for 5 min (b) buffer layer grown at $T=500$ °C for 3 min. The legends show the vertical dimension.

dominated mechanism. On the other hand, when the incoming flux is high, the chance of nucleation is increased and the possibility of the as-deposited nucleus to coalesce is also increased because of its larger density. This in turn promotes lateral growth and improves the surface roughness. One deals conceptually in this case with a nucleation-dominated mechanism. Under slow growth rate conditions, growth is controlled by ''growth-dominated'' mechanisms resulting in a rough buffer surface due to the large contact angle of the nuclei. When the growth rate increases, the nucleation rate also increases due to the large flux of impinging species.

Nucleation-dominated mechanisms control in this case the growth. Since the nucleation controlled growth mode promotes lateral growth, it results in improved surface morphology. This growth mechanism resembles in fact to that present under low-temperature conditions where a high nucleation rate is observed. Overall, it appears that a high growth rate is more suitable for growth of improved quality buffer layers.

V. AFM EVALUATION OF BULK GaN LAYERS GROWN ON BUFFERS OF DIFFERENT CHARACTERISTICS

After formation of the nucleation layer, the growth becomes homoepitaxial. Higher growth temperatures are consequently preferred for achieving surface thermal equilibrium and promoting lateral growth leading to 2D growth.[9] This suggests that once the substrate is covered by a thin nucleation layer, which acts as a buffer, the subsequent film should be grown at a higher temperature for improved quality. Growth should consequently take place in two steps. A thin buffer layer should first be grown at a low temperature, and then followed by a thick film grown at a higher temperature.

A two-step buffer growth approach was implemented as suggested by the results of the previous analysis. GaN films 0.5 μm thick were grown for this purpose on buffers realized using different growth parameters. X-ray diffraction measurements on such layers showed enhancement of the GaN cubic phase for films grown on optimized buffer layers as previously reported by the authors.[10] Figure 10 shows the morphology of the 0.5 μm GaN films as obtained by AFM. The films were grown on buffers which were realized at (a) 530 °C for 5 min and (b) 500 °C for 3 min. The latter corresponds in fact to the optimized growth parameters for buffer layers which were described in the previous sections. As can be seen, films grown on the optimized buffer layer show improved morphology. The morphology of the thick GaN films depends on the roughness of the nucleation layers; smooth buffer layers result in good morphology of the subsequently grown thick layers. The results of Fig. 10 indicate a roughness reduction from 360 to 320 Å, and a grain surface increase from 1.7×10^4 to 2.4×10^4 nm^2. Overall, it appears that growth on buffers realized under the optimized conditions of 500 °C/3 min results in better quality bulk GaN layer characteristics.

VI. CONCLUSION

The characteristics of GaN nucleation layers on (001) GaAs were studied by employing AFM and considering the associated growth kinetics. The morphology of the grown layers was found to depend on growth temperature, growth rate, and time and the best morphology is achieved by growth at 500 °C for 3 min. High growth rates also seem to favor the buffer morphology. Since growth becomes homoepitaxial once the substrate is entirely covered by the buffer, a higher temperature is necessary for 2D growth of the subsequent bulk layer. A two-step growth approach should therefore be preferred for (GaN) growth. Thick layers were finally grown on buffers realized by different growth conditions and the results demonstrate that the quality of the subsequently grown layer is controlled by the morphology of the buffer layer.

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