Surface kinetics of zinc-blende (001) GaN

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We study the relation between surface reconstruction transitions and surface kinetics for cubic GaN grown by plasma-assisted molecular-beam epitaxy on (001) GaAs. Reflection high-energy electron diffraction is used to monitor the transient behavior of the surface reconstruction upon the pulsed supply of either Ga or N at a given substrate temperature. We develop a model of the adsorption-diffusion-desorption kinetics of Ga and N adatoms to understand the dynamics of the surface reconstruction transitions quantitatively. Our results show that the surfaces phases of GaN constitute kinetic barriers for the decomposition of GaN, being of either energetic and entropic character depending on surface termination. [S0163-1829(96)03231-6]

The growth behavior of crystals is, in general, determined by both bulk thermodynamics and surface kinetics. However, for nonequilibrium conditions such as established during molecular-beam epitaxy (MBE) or metal-organic vapor-phase epitaxy (MOVPE), surface kinetics plays a major and often dominating role for growth. The reason for this fact is that the surface constitutes a two-dimensional phase in its own right, which has properties much distinct from the underlying bulk phase.[1–4] It is this surface phase which is responsible for the growth kinetics of the material.[5]

In this work, we study the surface kinetics of cubic GaN and its relation to epitaxial growth. GaN is a fascinating candidate for such studies for several reasons. First of all, its chemical properties drastically differ from those of other III-V compounds, in that it combines the apparently contradictory properties of a high ionicity (34%, i.e., larger than most II-VI compounds) and a large bond strength (10 eV, i.e., close to diamond). Consequently, its surface properties cannot easily be extrapolated from those of other III-V compounds.[6] Actually, even apparent bulk properties of GaN, such as its exceptionally high thermal stability, have puzzled researches for several decades.[7] The frequently quoted kinetic barriers for the dissociation of GaN (Ref. 8) are in fact yet to be understood, and are most likely related to the surface properties of GaN. Second, studies of the surface kinetics of GaN are definitely required for obtaining an improved understanding of its growth. MBE growth is commonly carried out at quite low temperatures ($0.3\times T_M$, where T_M is the melting point) compared to the MOVPE case. Such low temperature might be an actual prerequisite for stabilizing the cubic modification, but are also expected to impose limitations to the morphology one is able to obtain.[9]

In our previous work, we reported on the observation of three distinct surface reconstructions of cubic (001) GaN.[10] Here we study the surface reconstruction transitions of cubic GaN both experimentally and theoretically. The transition dynamics is monitored under isothermal conditions by *in situ* reflection high-energy electron diffraction (RHEED). We compare these experiments to simulations using a kinetic model which describes the reconstruction transitions in terms of the initial adsorption, diffusion, and subsequent evaporation of the respective surface species.

The GaN film used for this investigation is prepared on an exactly (001)-oriented GaAs substrate by MBE using a high-voltage ($\simeq 1.5$ kV) plasma glow-discharge N source. The growth procedure follows that described in Ref. 10. Surface reconstructions are monitored *in situ* by RHEED, using an incident angle of 3° and an acceleration voltage of 15 kV. The RHEED intensity is detected by a CCD camera, and analyzed by an image-processing system. The temperatures quoted in this paper are thermocouple readings following a three-point calibration, assuming (i) the (2×4)-$c(4\times4)$ reconstruction transition of GaAs to occur under an As_4 flux of 8×10^{-6} Torr at 490°C, (ii) the desorption of the native oxide of GaAs to take place at 580°C, and (iii) the growth rate of GaAs as measured by RHEED intensity oscillations to drop at temperatures above 630°C. The Ga flux is determined by RHEED intensity oscillations during GaAs buffer layer growth under N_2 background pressure. The N flux is obtained via *ex situ* measurements of the thickness of films grown under Ga-rich conditions.[11]

We begin with the phenomenology of the surface reconstruction transitions on GaN.[10] Briefly, we classify these reconstructions on the basis of the experimentally determined surface coverage and symmetry. In addition to the N-terminated (1×1) surface, (2×2)- and $c(2\times2)$-reconstructed phases were observed, which are linked to 0.5 and 1.0 ML of Ga coverage, respectively. The $c(2\times2)$-reconstructed surfaced was identified as the optimum one for achieving single-phase cubic growth. This surface, however, was found to be instable with respect to the (2×2)-reconstructed phase at intermediate coverage, which is stable in vacuum. In the course of this study, we found the latter statement to be true for annealing periods of up to 1 h at 680 °C. This finding is consistent with the slow dissociation kinetics of bulk GaN with respect to the equilibrium case.[7,8,12]

An impinging flux of either Ga or N onto the (2×2) surface leads to a transition to a $c(2\times2)$ or a (1×1) reconstruction, respectively. Measuring the intensity of the half-order reconstruction streak along a ⟨110⟩ azimuth allows us to record this phenomenon in real time. Figures 1 and 2 show selected examples of such time scans upon the pulsed supply of 1-ML N (Fig. 1) and 0.5-ML Ga (Fig. 2) for two different temperatures. The maximum intensity corresponds in each

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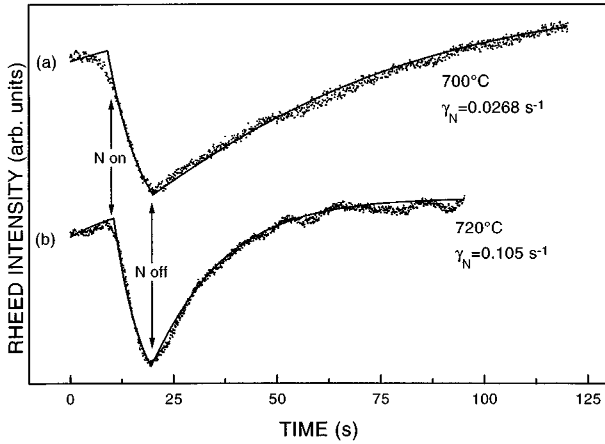

FIG. 1. RHEED intensity transient upon a 1.0-ML N dose at (a) 700 °C and (b) 720 °C. Solid squares represent experimental data, and solid lines show the best fit of Eq. (4). The time interval of N supply is indicated in the figure, as well as the desorption rates deduced from the fits.

case to that of the (2×2) reconstruction, while the intensity drop is associated with the transition toward either the (1×1)- or $c(2\times2)$-reconstructed surfaces (The former surface remains stationary for any amount of N supplied in excess of 1 ML). It is obvious from these experiments that the half-order streak first vanishes upon the impinging flux of both N and Ga, but recovers in a finite time once the supply has ceased. Note that the recovery time is substantially shorter at higher temperature. The simplest explanation for this effect consists in the initial adsorption of either N or Ga, thus forming surface phases distinct in coverage and symmetry from the (2×2) surface phase, followed by the isothermal desorption of the species building up these phases.

Assuming that these reconstruction transitions are caused by adsorption, diffusion, and desorption of the corresponding surface specie,[13] we next develop a—largely phenomenological—model for the surface kinetics of GaN. The model is required to account for adsorption and desorption of both Ga and N as well as for the formation of excess Ga, which eventually will form droplets, and for GaN growth in the case of the simultaneous presence of Ga and N. Moreover, there are three surface reconstructions distinct in both coverage and symmetry we have to deal with. Among them, the (2×2)- and $c(2\times2)$-related phases are supposed to be build up by one and the same surface species, namely, Ga dimers.[10] The stability difference between these phases could phenomenologically be described by a coverage-dependent desorption rate for Ga. Alternatively, and mathematically equivalent, we denote these two distinct surface constitutions of GaN by θ_1 and θ_2, respectively, where $0<\theta_i<0.5$ ML is to be satisfied. Our model, in units of ML's, is thus described by the equations

$$\frac{d}{dt}[\theta_1(t)]=2j_{\mathrm{Ga}}(\tfrac{1}{2}-\theta_1)+\hat{D}_{\mathrm{Ga}}\frac{(\frac{1}{2}-\theta_1)}{\theta_2}n+\gamma_{\mathrm{N}}(\tfrac{1}{2}-\theta_1)-j_{\mathrm{N}}\theta_1, \quad (1)$$

$$\frac{d}{dt}[\theta_2(t)]=2j_{\mathrm{Ga}}(\theta_1-\theta_2)+\hat{D}_{\mathrm{Ga}}\frac{(\theta_1-\theta_2)}{\theta_2}n-2\gamma_{\mathrm{Ga}}\theta_2-j_{\mathrm{N}}\theta_2, \quad (2)$$

$$\frac{d}{dt}[n(t)]=2j_{\mathrm{Ga}}\theta_2-\hat{D}_{\mathrm{Ga}}\frac{(\frac{1}{2}-\theta_2)}{\theta_2}n-2k_n n^{2/3}, \quad (3)$$

where θ_1 and θ_2 denote the Ga dimer coverage related to (2×2) and $c(2\times2)$ domains, n the amount of excess (liquid) Ga, j_{Ga} and j_{N} the Ga and N flux, $\hat{D}_{\mathrm{Ga}}$ the diffusion rate of excess Ga adatoms impinging onto θ_2, γ_{Ga} and γ_{N} the rates of Ga and N desorption, and k_n the rate coefficient of excess Ga desorption. The first term of each equation accounts for adsorption of Ga, building up the θ_1 phase and subsequently the accompanying phases θ_2 and n. In much the same way, the second terms account for diffusion of Ga adatoms impinging onto θ_2 domains having a size proportional to the coverage. In other words, the diffusion rate is defined as the ratio of diffusion coefficient D_{Ga} and domain size L^2. The third terms describe the desorption of N, Ga dimers (θ_2), and excess Ga (n), where the latter phase has been assumed eventually to form hemispherical droplets where desorption takes place from the droplet's surface which is of order $\frac{2}{3}$. The last terms in Eqs. (1) and (2), finally, stand for the incorporation of Ga and N adatoms into the crystal, i.e., actual growth.[14] Note that the model described by Eqs. (1)–(3) is a linearized and highly simplified version of microscopic theories of the surface kinetics such as developed in Ref. 13. This simplification is necessary to reduce the number of free parameters and thus to guarantee stable fits, but also means that, while our model is perhaps the most simple one accounting for the phenomena we wish to describe, there certainly are a variety of more refined models which could equally well describe the data.

Finally, we have to relate the surface coverage calculated by means of Eqs. (1)–(3) to the quantity experimentally observed, namely, the RHEED intensity. Although the intensity

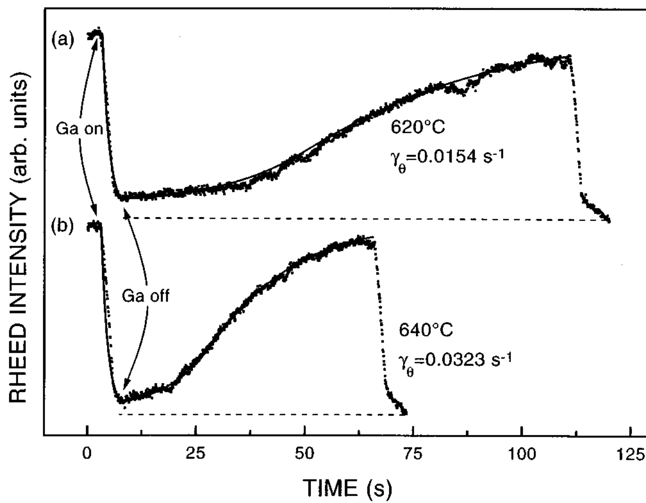

FIG. 2. RHEED intensity transient upon a 0.5-ML Ga dose at (a) 620 °C and (b) 640 °C. Solid squares represent experimental data, and solid lines show the best fit of Eq. (4). The dashed lines show the zero level which is defined by the half-order beam intensity equaling the background intensity. The time intervals of Ga supply are indicated in the figure, as well as the desorption rates deduced from the fits.

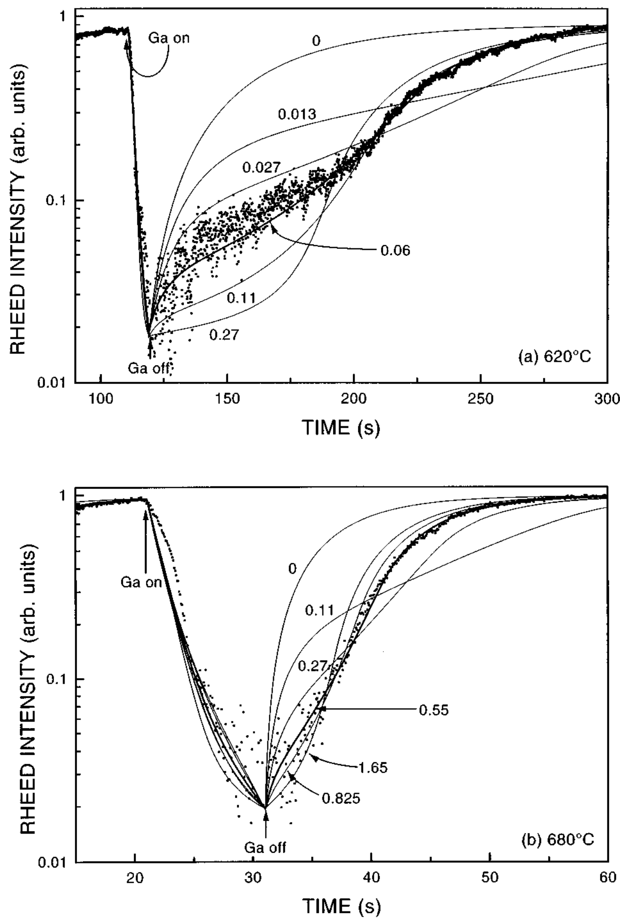

FIG. 3. Logarithmic display of RHEED intensity transients upon a 1.5-ML Ga dose at (a) 620 °C and (b) 680 °C. Solid squares represent experimental data, and the bold solid lines show the best fit of Eq. (4) using diffusion rates of (a) 0.06 s and (b) 0.55/s. The other lines show simulations assuming various other values for the diffusion rate $\hat{D}_{\mathrm{Ga}}$ as indicated at each curve. The time intervals of Ga supply are indicated in the figures.

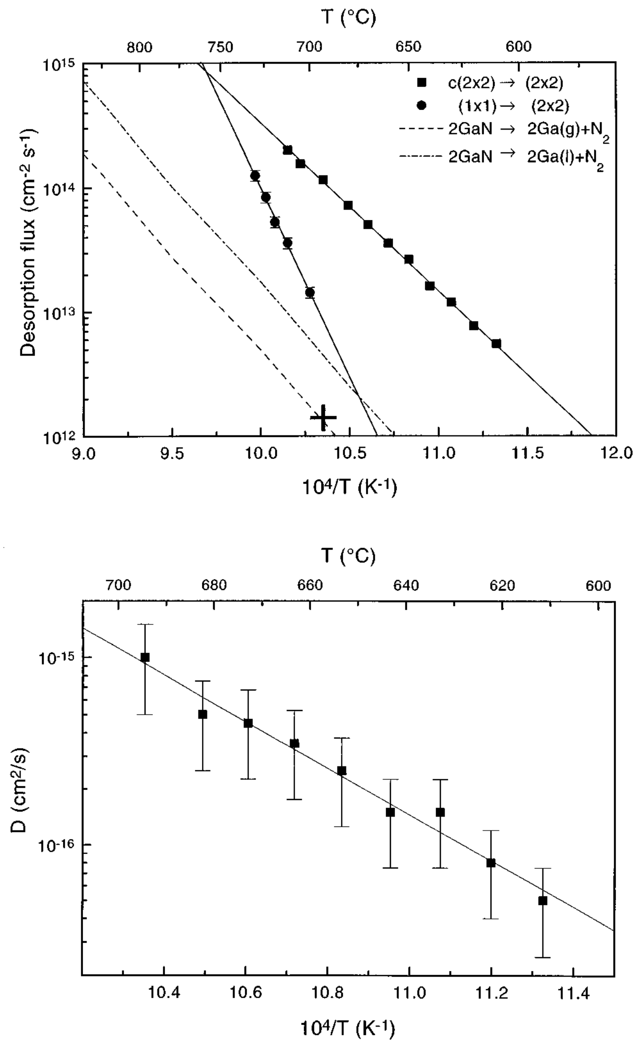

FIG. 4. Arrhenius representation of (a) the N and Ga desorption fluxes and (b) the diffusion coefficient D_{Ga}. The points are experimental data. For (a), solid squares refer to Ga, while the solid circles indicate values for N. The cross marks the lower limit for the stability of the (2×2)-reconstructed surface. The solid lines are least-square fits of single exponentials to our data. The dashed and dashed-dotted lines in (a) represent the data of Refs. 7 and 12 for the free-surface evaporation of GaN. For the Ga and N desorption flux (a), the fits result in Arrhenius parameters $\ln Z_0$ and E_a ($\ln Z_0 - E_a/k_BT$) of 64.5±0.6 and 2.69±0.05 eV and 102±2 and 6.1±2 eV, respectively. For the diffusion coefficient D_{Ga}, we obtain $D_0 = 0.007$ cm^2/s and $E_d = 2.48$ eV, where $D_{\mathrm{Ga}} = D_0 \exp(-E_d/k_BT)$.

in RHEED is, in general, to be calculated by dynamical diffraction theory, here we use the kinematical approximation to perform the simulations in a reasonable amount of time.[15] Within the kinematical approximation,[16] for the intensity of the half-order reconstruction streak along a ⟨110⟩ azimuth we thus write

$$I_{\langle 110\rangle}(t) = [\theta_1(t) - \theta_2(t)]^2. \quad (4)$$

Simulations based on Eqs. (1)–(4) are shown in Figs. 1 and 2 together with the corresponding experimental data, the latter of which were normalized to 1 with the zero level defined by the simultaneously recorded background intensity. The simulations are fit to the data by a numerical least-square routine (conjugate gradient), and the fits were found to be stable regardless the values of the initial parameters.[14] Since these RHEED transients are actually a measure of the isothermal desorption rate as a function of coverage, the good agreement of the experimental and simulated transients reveals that desorption of both N and Ga is a *first-order* process. A closer examination of Fig. 2 reveals that during the first (0.5 ML) supply of Ga the RHEED intensity does actually not drop to zero (dashed lines), i.e., the coverage of θ_2 is incomplete. Apparently, excess Ga is formed parallel to the θ_2 phase before the latter is completed. This finding indicates a comparatively small diffusion rate of Ga adatoms.

Figure 3 shows RHEED transients at (a) 620 °C and (b) 680 °C upon the supply of 1.5-ML Ga on a logarithmic scale. The amount of excess Ga is larger and, thus, the influence of its diffusion is more pronounced than for the 0.5-ML does shown above. The experimental data are compared to simulations where all parameters have been kept constant except for the diffusion rate $\hat{D}_{\mathrm{Ga}}$. The sensitive dependence of the transient behavior on this parameter is evident.

Figure 4(a) shows the desorption fluxes derived from our simulations in an Arrhenius representation. The volatility of

both Ga- and N-related surface phases is, in the investigated temperature range, on the same order of magnitude as that observed for the free evaporation of bulk GaN. The stability of all surface phases is many orders of magnitude higher than expected under equilibrium conditions,[17] showing that in all cases desorption is greatly kinetically hindered. Interestingly, at temperatures below 760 °C, Ga is the more volatile species at the growth front rather than N.

In Fig. 4(b), we present the temperature dependence of the diffusion coefficient D_{Ga}.[18] The diffusivity is characterized by an activation energy of 2.48 eV. Note that this activation energy may originate from the temperature dependence of the domain size L^2, which is determined by diffusion of Ga on the (2×2)-reconstructed surface, rather than by D_{Ga}, which accounts for diffusion of excess Ga on the $c(2\times2)$ domains.

In conclusion, our analysis has several important implications.

(i) The surface phases of GaN represent a large kinetic barrier for evaporation, particularly the (2×2)-reconstructed phase. The large difference in the preexponential terms and in the apparent energies of evaporation between Ga- and N-related surface phases means that these kinetic barriers are of both entropic and energetic character. The stability of the N-terminated surface is perhaps related to a steric effect: Dimerization of N, which would greatly enhance the volatility of this surface, is prevented by the remoteness of chemisorbed N adatoms relative to their covalent radius.

(ii) The diffusivity of Ga on (001) GaN is governed by a large energy of activation. This finding is consistent with arguments predicting a scaling of surface diffusivity with the cohesive strength of the material.[9]

(iii) Under MBE growth conditions, the surface stoichiometry during growth is severely influenced by Ga desorption. This phenomenon intricates the growth of single-phase cubic GaN films, where the slightest deviation from the optimum surface stoichiometry induces the nucleation of the hexagonal phase.[10] Furthermore, the diffusivity of Ga at MBE growth temperatures is low, which presumably inhibits the formation of truly smooth surfaces.

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[14] For the experiments presented in this work, Eqs. (1)–(3) actually simplify considerably. Since only one species, say, N, is impinging onto an initially (2×2)-reconstructed surface, most terms of the equation system are actually zero, and the temporal evolution of the surface is exclusively determined by j_N in the adsorption stage and by γ_N in the desorption stage. The equivalent statement applies for the case of Ga impinging onto the (2×2) surface, except that in this case the formation of excess Ga (n) may come into play.

[15] Calculations based on a semikinematical model which includes dynamical diffraction effects by the inner potential of the crystal were also performed, and were found to be in good agreement with the kinematical calculations presented throughout this paper [W. Braun, O. Brandt, H. Yang, and K.H. Ploog (unpublished)]. The adatom coverage θ was simulated by constructing supercells of up to ten times the unit mesh size, covering the range between 0.1–0.9-ML Ga coverage. The computation time required for calculating the RHEED intensity for one specified coverage varies between 10 and 100 min on a Sun Sparc 10/42 workstation, depending on the size of the supercell.

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[18] The determination of $D_{Ga}=\hat{D}_{Ga}L^2$ requires knowledge of the domain size L, which is acquired here by scanning tunneling microscopy investigations of our GaN films. These studies show that the surface reconstruction is disordered on an atomic scale. As a worst-case approximation, the surface domain size L^2 has been assumed to be on the order of one unit cell. This assumption results in a preexponential term of 0.007 cm^2/s, which is in fact consistent with the expected ''universal'' $D_0\sim\nu/4N_0$, where ν is the frequency of thermal vibrations and N_0 is the surface-site density.