PHYSICAL REVIEW B VOLUME 55, NUMBER 11 15 MARCH 1997-I

Simulation of GaAs growth and surface recovery with respect to gallium and arsenic surface kinetics

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(Received 21 August 1996; revised manuscript received 1 November 1996)

A Monte Carlo simulation of GaAs homoepitaxy and subsequent surface recovery is performed using a solid-on-solid configuration. It is assumed that both Ga atoms and GaAs molecules are mobile during growth and contribute to the surface-diffusion flux. When growth is terminated by stopping the Ga supply, all Ga adatoms are found to react very quickly to form GaAs molecules. Thus, during recovery only diffusion of less mobile GaAs molecules is of relevance. The simulation is parametrized by a detailed comparison with reflection high electron energy diffraction measurements. In particular, the recovery phase after growth stops, the oscillation damping, and the As_4 sticking coefficient are analyzed. Quantitative agreement with all measurements is achieved and a simulation of the flux-ratio-dependent behavior is possible, as is demonstrated for the As_4 sticking coefficient. [S0163-1829(97)00512-2]

I. INTRODUCTION

Molecular beam epitaxy (MBE) is well established as a technology for the fabrication of nanometer scale structures. Controlled growth of sophisticated structures requires fundamental knowledge of the detailed atomic processes such as adsorption, desorption, migration, and reaction. Investigations of the GaAs surface kinetics during growth were performed by using experimental methods such as reflection high energy electron diffraction[1–4] (RHEED) and scanning tunneling microscopy[5,6] (STM) measurements. The results are discussed with theoretical methods such as analytical calculations[7,8] and Monte Carlo simulations.[9–11] In particular, the combination of computer simulations and RHEED measurements is found to be a very powerful tool for the investigation of the basic processes during crystal growth. As an important result, Shitara *et al.* observed an approximately linear relationship between simulated surface step densities and measured values of the intensity of the RHEED specular beam over a wide range of growth conditions.[11] Consequently, the chronological evolution of simulation runs can be compared directly with real growth processes. However, quantitative reproduction of the surface recovery after growth stops appears problematic.[11] To solve this problem, a step edge barrier was introduced, which hampers interlayer migration and yields correct recovery.[12] Nevertheless, surfaces simulated by this extended model show a mountainous structure[13] which is not found experimentally.[6]

Here we present an alternative approach to a realistic simulation of GaAs growth and surface recovery without the need of a step barrier. In our simulation we include surface kinetics of gallium and arsenic. The model reproduces the recovery correctly, realistic surface structures are obtained, and, in addition, simulation of the flux-ratio-dependent behavior is possible, as is demonstrated for the As_4 sticking coefficient.

II. EXPERIMENTAL SETUP

The growth experiments are performed in a MBE system described in a former paper.[14] As a peculiarity, a quadrupole mass spectrometer allows precise control of the As_4 flux and of the Ga/As flux ratio. Growth is carried out on nominally planar (001) GaAs substrates. After the oxide removal by heating up the surface under arsenic pressure, a 300 nm thick buffer layer is grown in order to smooth the surface. During growth of the subsequent layers, the RHEED specular beam intensity along the [110] azimuth is recorded by a sensitive CCD camera in combination with a frame grabber and a personal computer for image processing. With in-phase diffraction conditions the modulation of the specular beam intensity during growth can be traced back to variations of the surface step density only.[11]

III. SIMULATION MODEL

The simulation used here closely resembles a model presented by Clarke and Vvedensky.[10] With this model, Shitara *et al.* successfully simulated epitaxial growth on GaAs (001) surfaces.[11] Basic assumptions are a cubic lattice, a solid-on-solid configuration[15] (that means no overhangs and no vacancies), random deposition as well as surface migration of gallium. As an extension to the basic model, our simulation includes surface kinetics of Ga and As atoms, and GaAs molecules. Arsenic incorporation is modeled by a process in which every impinging As_4 molecule dissociates into atoms. Two As atoms desorb resulting in a maximum As_4 sticking coefficient of 0.5.[16] The two remaining As atoms perform a random search for a free gallium atom and either react to GaAs or desorb as well.

After impinging, the adsorbants move randomly by isotropic nearest-neighbor hopping. The hopping rate of an adsorbant is given by

$$k(T)=k_0\exp\left(-\frac{E_{\mathrm{dif}}}{k_BT}\right), \tag{1}$$

where $k_0=1\times10^{13}\ \mathrm{s}^{-1}$ is assumed as a vibrational frequency, k_B is Boltzmann's constant, T is the substrate temperature, and the surface diffusion barrier is[11]

$$E_{\mathrm{dif}}=E_S+nE_N, \tag{2}$$

with the surface contribution E_S, the number of nearest-neighbors $n=0,\ldots,4$, and the nearest-neighbor contribution E_N.

Surface diffusion of Ga atoms, As atoms, and GaAs molecules is taken into account. As a simplification, the migration of GaAs molecules is modeled by the same mechanism as for diffusion of single atoms. Just the diffusion barrier is supposed to be significantly higher. The surface contributions E_S for Ga, As, and GaAs are denoted as $E_{S,\mathrm{Ga}}$, $E_{S,\mathrm{As}}$, and $E_{S,\mathrm{GaAs}}$, respectively. To reduce the number of simulation parameters, the same value of the nearest-neighbor contribution E_N is used for Ga atoms and GaAs molecules. Arsenic migration is simulated in a special manner. Due to the short lifetime of arsenic on the surface,[17] no arsenic-arsenic interactions are considered. Thus, every migrating As atom can be treated separately. Interaction of As atoms with GaAs molecules is neglected, whereas interaction with Ga atoms results in reaction to GaAs molecules. Arsenic atoms may desorb when they find no Ga atom within their surface lifetime. Desorption of Ga atoms and GaAs molecules is neglected due to the gallium sticking coefficient of unity up to temperatures of 620 °C.[18]

The characteristic quantity to describe migration of As atoms is the surface-diffusion length up to desorption: $\lambda_{\mathrm{As}}=\sqrt{D_s\tau_{\mathrm{des}}}$, with the surface-diffusion coefficient $D_s=(1/4)(a_0)^2k_0\exp(-E_{\mathrm{dif}}/k_BT)$ and the distance of a nearest-neighbor hopping a_0. With the above values we get

$$\lambda_{\mathrm{As}}=\left(\frac{a_0}{2}\right)\exp\left(\frac{dE_{\mathrm{As}}}{2k_BT}\right) \tag{3}$$

with $dE_{\mathrm{As}}=E_{\mathrm{des}}-E_{\mathrm{dif}}$,

The simulation is thus characterized by four parameters: $E_{S,\mathrm{Ga}}$, $E_{S,\mathrm{GaAs}}$, E_N, and dE_{As}. These quantities are to be regarded as effective diffusion barriers that incorporate in an average way local fluctuations, fast processes not included explicitly, and other factors such as surface reconstruction.[11] We would like to note that the values of these effective simulation parameters may change, if a more elaborate model with, for example, a zinc blende lattice and a reconstructed surface is considered.[19,20] However, at this point we would like to stick to the simple cubic model of Clarke and Vvedensky in order to keep the number of free parameters low.

As described below, detailed comparisons to RHEED measurements are made to determine the model parameters. Due to the [110] azimuth of the RHEED experiments, the numerical values of the energy barriers mainly reflect surface migration perpendicular to the orientation of arsenic dimers as well as bonds to gallium terminated steps.[21] Furthermore, three growth parameters are important: the growth temperature T, the growth rate G, given by the gallium flux, and the flux ratio $J_{\mathrm{Ga}}/J_{\mathrm{As}_4}$. All growth simulations are started on a 230 × 230 matrix without steps.

IV. RESULTS

In order to compare simulation results with real growth and recovery processes, surface step densities n_{st} are simulated and measured RHEED specular beam intensities I_{sp} are recorded. Shitara *et al.* pointed out that there is an approximately linear relationship between both quantities over a wide range of growth conditions.[11] An example of the experimentally observed time evolution of the specular beam intensity during growth and subsequent surface recovery is plotted in Fig. 1(a). The simulation of the corresponding step density is shown in Fig. 1(b). As can be seen, simulation and real growth yield nearly identical oscillations. One main difference is noticeable: the initial fast decrease after growth starts is smaller for RHEED oscillations than in the simulated step densities. This may reflect a change of reconstruction which is not included in the model.

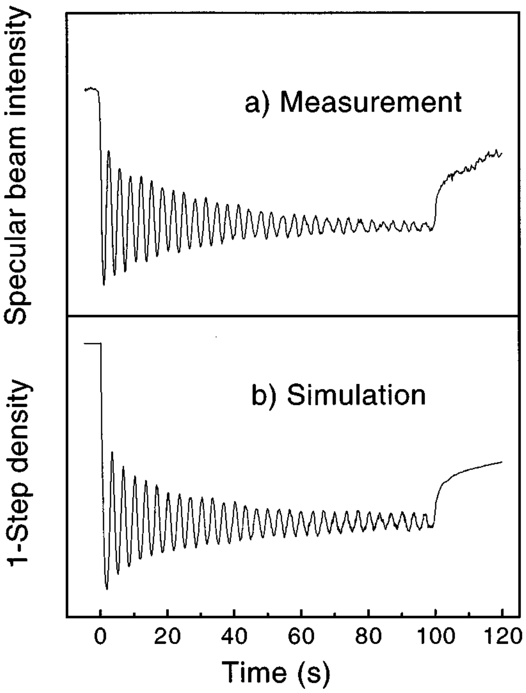

FIG. 1. Typical measured RHEED intensity oscillations (a) and simulated step density oscillations (b), with growth parameters: temperature T = 600 °C, growth rate G = 0.3 ML/s, and flux ratio $J_{\mathrm{Ga}}/J_{\mathrm{As}_4}$= 0.62, and simulation parameters: $E_{S,\mathrm{Ga}}$ = 1.39 eV, $E_{S,\mathrm{GaAs}}$ = 1.74 eV, E_N = 0.435 eV, and dE_{As} = 0.868 eV as are described in the text.

The parameters of the simulation are adjusted for maximum agreement with the RHEED measurements. For that purpose, the surface recovery behavior, the oscillation damping during growth, and the As_4 sticking coefficient are analyzed quantitatively. An initial surface for the recovery phase studies is created by deposition of 30 ML. According to Neave *et al.*,[1] the transients of n_{st} and I_{sp} after growth stops are fitted by the expression $I=A_0+A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$, where A_i are constants and τ_1 and τ_2 are the time constants of the fast and slow stage. Due to the unsystematic behavior of τ_2,[1] only the fast stage τ_1 is used for quantitative analysis. A series of simulation runs with varied values of the simulation parameters show that τ_1 is strongly dependent on $E_{S,\mathrm{GaAs}}$ and E_N, whereas $E_{S,\mathrm{Ga}}$ and dE_{As} do not affect the fast stage of the recovery phase significantly. This behavior is explained by the reaction of all mobile Ga atoms on the surface to GaAs molecules directly after the Ga supply is stopped. The time constant of this reaction is found

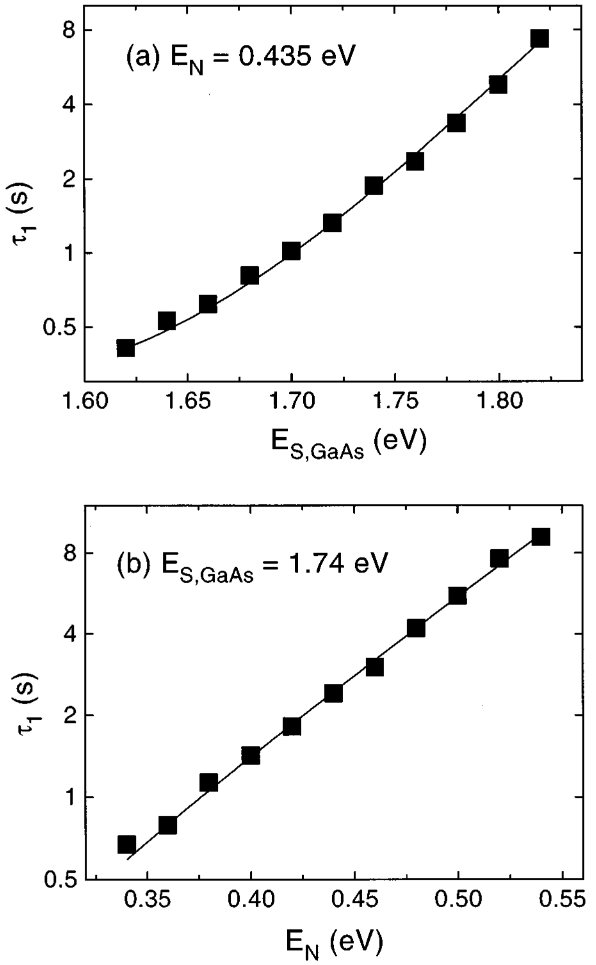

FIG. 2. Dependence of the fast stage of simulated recovery phases on (a) $E_{S,\mathrm{GaAs}}$ and (b) E_N. To determine τ_1, the surface recovery is fitted by the function: $I=A_0+A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$. Due to the unsystematic behavior of τ_2, only τ_1 is analyzed quantitatively. An initial surface for recovery studies is created by deposition of 30 ML.

to be about 0.05 seconds and, therefore, very small when compared to τ_1, which is in the range of several seconds. Thus, during recovery only surface migration of GaAs molecules and the corresponding energy terms are of relevance. In Fig. 2, τ_1 is plotted as function of E_N and $E_{S,\mathrm{GaAs}}$. Approximately exponential dependencies are found. An experimental value of τ_1 can be simulated by using several combinations of $(E_{S,\mathrm{GaAs}},E_N)$. To determine the correct combination, the temperature dependent behavior of τ_1 is analyzed. The inset in Fig. 3 shows values of τ_1 taken from RHEED measurements at different surface temperatures. Based on these measured values of τ_1, possible combinations $(E_{S,\mathrm{GaAs}},E_N)$ are determined from simulation runs with varied conditions (Fig. 3). From these data, the combination $(E_{S,\mathrm{GaAs}},E_N)$ which correctly represents the measurements is determined unequivocally. The best agreement at all temperatures is found for $E_{S,\mathrm{GaAs}}=1.74$ eV and $E_N=0.435$ eV. The value of E_N appears to be very high when compared to the value of 0.24 eV as proposed by Shitara *et al.*[11] To explain this difference, the respective experimental conditions are important. Shitara *et al.* analyzed the growth mode transition from two-dimensional nucleation to step flow growth in [010] azimuth to parametrize their simulation. Thus, their value of E_N is determined during the growth phase and represents an average given by bonds of both Ga atoms and GaAs molecules to gallium terminated steps as well as to arsenic terminated steps. In contrast to this, our value is determined from the post growth recovery behavior in [110] azimuth and reflects bonds of only GaAs molecules to gallium terminated steps.

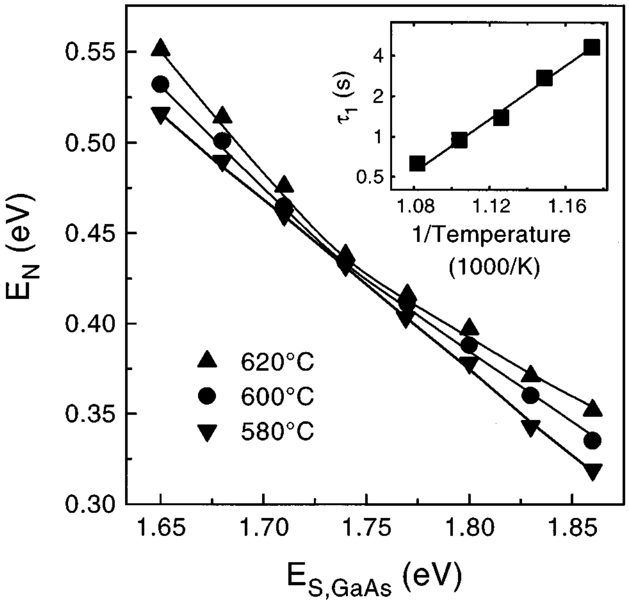

FIG. 3. Possible combinations of $(E_{S,\mathrm{GaAs}},E_N)$ giving the correct value of τ_1. The temperature dependence of τ_1 during real recovery processes is determined from RHEED measurements and is shown in the inset. Every data point $(E_{S,\mathrm{GaAs}},E_N)$ represents a set of at least eleven simulation runs as demonstrated in Fig. 2. The best agreement between simulation and measurement is obtained with $E_{S,\mathrm{GaAs}}$ = 1.74 eV and E_N = 0.435 eV.

The next stage contains the determination of $E_{S,\mathrm{Ga}}$ and dE_{As}. The Ga diffusion barrier is fixed by a quantitative analysis of the oscillation damping behavior. To characterize the oscillation damping, a damping constant ξ is introduced as the number of monolayers (ML) which can be deposited until the oscillation amplitude is reduced to the fraction of 1/*e* of the initial amplitude. Figure 4 shows the damping constant of simulated step density oscillations as a function of $E_{S,\mathrm{Ga}}$. More strongly damped oscillations with increasing values of $E_{S,\mathrm{Ga}}$ are found. This is assumed to be a result of the reduced surface migration of the Ga atoms and will be part of further investigations. The best agreement with the RHEED oscillation damping constant at the same growth conditions is found for $E_{S,\mathrm{Ga}}$ = 1.39 eV.

Measurements of the As_4 sticking coefficient are performed by using quadrupole mass spectroscopy and the frequency of RHEED oscillations as described in a former paper.[22] The value of dE_{As} is adjusted to reproduce the As_4 sticking coefficient. A value of dE_{As} = 0.868 eV yields agreement with the measurements in the regime of stoichiometric growth up to flux ratios $J_{\mathrm{Ga}}/J_{\mathrm{As}_4}$ of about 0.95 (Fig. 5). The perfect reproduction of the experimental data indicates the validity of the arsenic incorporation model.

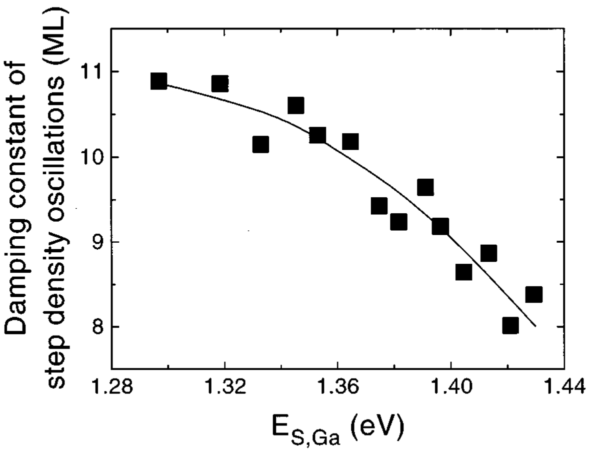

FIG. 4. Damping constant of simulated step density oscillations dependent on $E_{S,\mathrm{Ga}}$. The damping constant is given by the number of monolayers (ML) which can be grown until the oscillation amplitude is reduced to the value $1/e$ of the initial amplitude. Agreement with the measured value of 9.4 ML is found with $E_{S,\mathrm{Ga}} = 1.39$ eV.

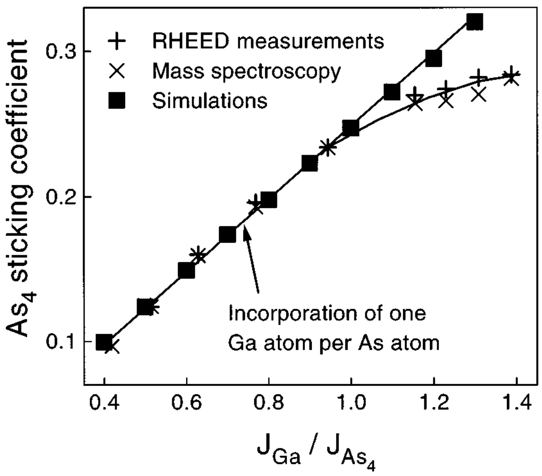

FIG. 5. Sticking coefficient of As_4 versus flux ratio. The data are obtained by RHEED measurements, mass spectroscopy, and by growth simulations. Stoichiometric growth is found up to flux ratios of about $J_{\mathrm{Ga}}/J_{\mathrm{As}_4}= 0.95$, higher flux ratios yield unstoichiometric films (Ref. 22).

The behavior at higher flux ratios is not perfectly reflected in the model. In experiment, unstoichiometric growth was found.[22] Our model only accounts for the formation of arsenic vacancies. The discrepancy between real growth in the unstoichiometric regime and simulations indicates that As vacancy formation is not the dominant mechanism. Other mechanisms such as antisite defects or the formation of gallium droplets are not implemented.

V. DISCUSSION AND CONCLUSIONS

As an important result, Shitara *et al.*[11] achieved quantitative agreement between simulation and experiment for the growth mode transition between two-dimensional nucleation and step flow growth. They considered surface diffusion of only gallium atoms and describe this process by an effective diffusion barrier which is valid only for a fixed Ga/As flux ratio. The model reproduces the growth phase correctly, but recovery after growth stops was found to be too fast when compared to RHEED measurements. An attempt to better simulate both phases was presented by Smilauer and Vvedensky.[12] To hinder interlayer migration and, thus, slow down the simulated recovery, a step edge barrier was introduced in combination with short-range incorporation of freshly deposited Ga atoms which results in a smoothing of the growing surface. With these extensions, recovery was simulated correctly, but surfaces created by this modified model show a mountainous structure unlike the experiment.[13]

The model presented here is an alternative approach to a realistic simulation of GaAs growth and recovery without a step edge barrier. We improve the model of Shitara *et al.*[11] with regard to varied flux ratios. Thus, we take into account the experimental fact that after gallium supply is terminated, the Ga/As flux ratio changes drastically. In our model, not only Ga atoms but also GaAs molecules migrate on the surface during growth. Surface diffusion of chemisorbed molecules is a known process and was observed, for example, by Xiao *et al.*[23] for diffusion of CO on Ni surfaces. Yet, to our knowledge, no investigations of surface diffusion of GaAs molecules on GaAs surfaces were made. Most importantly, after growth stop, all Ga adatoms are found to react very quickly to less mobile GaAs molecules resulting in a slowed recovery. With this assumption, we are able to succesfully model the recovery phase.

The effect of the slowly migrating GaAs molecules in our model is similar to the effect of step edge barriers for Ga migration in the model of Smilauer and Vvedensky,[12] whereas the effect of the rapidly migrating Ga atoms in our model is similar to the effect of short-range incorporation of freshly deposited gallium. Both models can be used to repro-

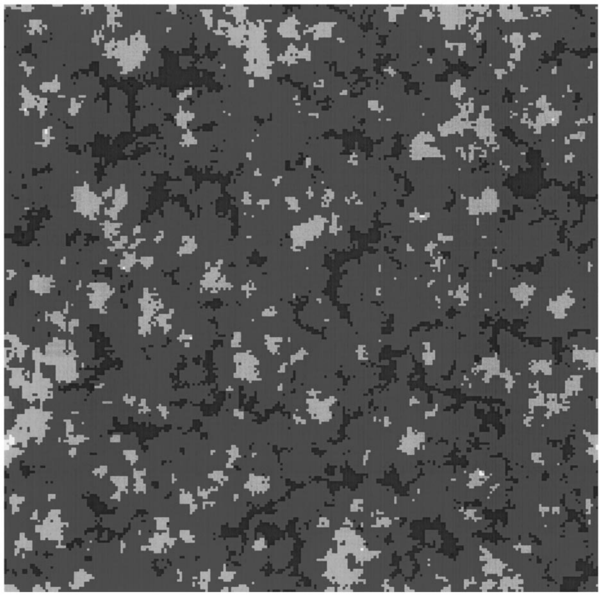

FIG. 6. Typical simulated surface after deposition of 30 ML. Deeper areas are colored darker and higher areas lighter, each color represents one monolayer. The size of the simulation field is 230 × 230 sites representing a surface area of 92 × 92 nm.

duce the time-dependent behavior of the RHEED specular beam intensity during growth and recovery. Nevertheless, the introduction of a step edge barrier yields a significant change of the surface morphology.[13] Surfaces simulated without step edge barriers are similar to small area STM pictures of real surfaces as shown, for example, in Ref. 6. A typical surface morphology produced with our model is shown in Fig. 6. As can be seen, two-dimensional growth islands with monolayer height and holes are the dominant features on the surface, but no mounds are visible. This morphology can be understood in the picture of the layer-by-layer growth model.[1]

In contrast, applying a step edge barrier, the resulting surfaces showed mountainous features with a lateral size of about 10 to 20 nm.[24] The formation of these simulated multilayer mounds cannot be explained with the layer growth model. In Ref. 13, mound generation was attributed to the hindered downward migration of adatoms at step edges. The introduction of a step edge barrier results in the occupation of new layers. However, a corresponding growth of such nanometer mounds is not found in STM pictures.[6] On the other hand, we imply for our simulation model that a step edge barrier is *not* necessary to explain the recovery phase. Assuming slowly migrating GaAs molecules we can explain the recovery phase as well as the absence of multilayer mounds in STM measurements.

We would like to note that with atomic force microscopy scanning larger surface areas as compared to the STM measurements[6] unstable growth and the formation of large mounded structures with a micrometer lateral size and a height of several nanometers was found.[25,26] These results may indicate that a step edge barrier could be important for the correct simulation of the topology of large areas. But the energy barrier is probably much smaller than the value proposed by Smilauer and Vvedensky.[12] Furthermore, RHEED measurements should not be affected significantly by these micrometer structures since their lateral size is at least one order of magnitude larger than the coherence zone of the electron beam.

In addition, with our model simulation of the flux-ratio-dependent behavior is possible, as is demonstrated for the As_4 sticking coefficient. Detailed investigations of the influence of the flux ratio on GaAs homoepitaxy will be presented in a future paper.

ACKNOWLEDGMENTS

We would like to thank R. Anton, A. A. Schmidt, T. Franke, and W. Hansen for helpful discussions and the Deutsche Forschungsgemeinschaft for their support by providing parts of the experimental equipment and personal funds.

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[1] J. H. Neave, B. A. Joyce, P. J. Dobson, and N. Norton, Appl. Phys. A **31**, 1 (1983).

[2] J. H. Neave, P. J. Dobson, B. A. Joyce, and J. Zhang, Appl. Phys. Lett. **100**, 47 (1985).

[3] T. Nishinaga, T. Shitara, and M. Mochizuki, J. Cryst. Growth **99**, 482 (1990).

[4] L. Däweritz, J. Griesche, R. Hey, and J. Herzog, J. Cryst. Growth **111**, 65 (1991).

[5] M. D. Pashley, K. W. Haberem, and J. M. Gaines, Appl. Phys. Lett. **58**, 406 (1991).

[6] J. Sudijono, M. D. Johnson, M. B. Elowitz, C. W. Snyder, and B. G. Orr, Surf. Sci. **280**, 247 (1993).

[7] A. K. Myers-Beagton and D. D. Vvedensky, J. Cryst. Growth **111**, 162 (1991).

[8] A. Zangwill, C. N. Luse, D. D. Vvedensky, and M. R. Wilby, Surf. Sci. **274**, L529 (1992).

[9] A. Madhukar and S. V. Ghaisas, CRC Crit. Rev. Solid State Mater. Sci. **14**, 1 (1988).

[10] S. Clarke and D. D. Vvedensky, Phys. Rev. Lett. **58**, 2235 (1987).

[11] T. Shitara, D. D. Vvedensky, M. R. Wilby, J. Zhang, J. H. Neave, and B. A. Joyce, Phys. Rev. B **46**, 6815 (1992).

[12] P. Smilauer and D. D. Vvedensky, Phys. Rev. B **48**, 17 603 (1993).

[13] D. D. Vvedensky, P. Smilauer, and T. Shitara, in *Nanostructures and Quantum Effects*, edited by H. Sakaki and H. Noge, Springer Series in Materials Sciences Vol. 31 (Springer-Verlag, Berlin, 1994), pp. 285–293.

[14] Ch. Heyn and M. Harsdorff, J. Cryst. Growth **133**, 241 (1993).

[15] J. D. Weeks and G. H. Gilmer, Adv. Chem. Phys. **40**, 157 (1979).

[16] C. T. Foxon and B. A. Joyce, Surf. Sci. **50**, 434 (1975).

[17] C. T. Foxon and B. A. Joyce, Acta Electron. **21**, 139 (1978).

[18] J. Ralston, G. W. Wicks, and L. F. Eastman, J. Vac. Sci. Technol. B **4**, 594 (1986).

[19] J. M. McCoy and P. A. Maksysm, J. Cryst. Growth **111**, 178 (1991).

[20] T. Ito and K. Shiraishi, Surf. Sci. **357**, 486 (1996).

[21] T. Shitara, D. D. Vvedensky, M. R. Wilby, J. Zhang, J. H. Neave, and B. A. Joyce, Phys. Rev. B **46**, 6825 (1992).

[22] Ch. Heyn and M. Harsdorff, J. Cryst. Growth **150**, 117 (1995).

[23] Xu-Dong Xiao, X. D. Zhu, W. Daum, and Y. R. Shen, Phys. Rev. Lett. **66**, 2352 (1991).

[24] P. Smilauer and D. D. Vvedensky, Phys. Rev. B **52**, 14 263 (1995).

[25] M. D. Johnson, C. Orme, A. W. Hunt, D. Graff, J. Sudijono, L. M. Sander, and B. G. Orr, Phys. Rev. Lett. **72**, 116 (1994).

[26] C. Orme, M. D. Johnson, K. T. Leung, B. G. Orr, P. Smilauer, and D. D. Vvedensky, J. Cryst. Growth **150**, 128 (1995).