

# **Atomistic Basis for Continuum Growth Equation: Description of Morphological Evolution of GaAs During Molecular Beam Epitaxy**

T. Tiedje<sup>1</sup>, A. Ballestad<sup>2</sup>

Department of Physics and Astronomy, <sup>1</sup>also Department of Electrical and Computer Engineering, University of British Columbia, Vancouver, BC, V6T 1Z4

## **Abstract**

This review brings together experimental data on surface shape evolution during epitaxial growth of GaAs with kinetic Monte Carlo simulations of a solid-on-solid model and numerical solutions of a continuum growth equation derived from an adatom transport equation. Scanning probe and light scattering measurements of the surface morphology of GaAs, grown by molecular beam epitaxy, on planar as well as patterned (100) substrates are reviewed. We show that the experimental data can be described by a stable continuum growth equation that is mixed-order in the spatial derivatives, with an Edwards-Wilkinson type linear term, together with a conservative nonlinear term. The stable growth equation is derived from two coupled rate equations, one of which describes the transport of adatoms on the surface and the other describes the rate of change of surface height due to adatom incorporation into the surface at step edges. In this analysis, we assume that there is a combination of an Ehrlich-Schwoebel barrier and/or an incorporation barrier at step edges that favor a net downhill migration of adatoms across step edges, with the consequence that the growth model, like the experimental system, is stable, meaning that undulations in the surface tend to smooth out during growth. The coefficients in the growth equation depend on the growth rate and the density of steps on the surface. The continuum description of the morphological evolution is tested by comparisons to computer experiments consisting of kinetic Monte Carlo simulations of a solid-on-solid model. The methods used in this analysis of GaAs epitaxy are expected to be broadly applicable to other materials that exhibit stable epitaxial growth.

<sup>2</sup> Present address: BC Cancer Agency, Vancouver, BC

## 1. Introduction

Epitaxial crystal growth is an atomic self-assembly process in which the shape of the grown surface is one of the significant outcomes. Even though epitaxy is a simple example of self-assembly compared to, for example, the self-organization that takes place in biological systems, nevertheless it is still remarkably complex with numerous, as yet unanswered questions. There is a shortage of good experimental data on surface shapes for epitaxial growth that allows a quantitative comparison to be made with the predictions of atomistic and continuum models of the growth process. In this review, we bring together a variety of experimental results on surface shapes of GaAs for the case of homoepitaxial growth on both planar and patterned surfaces by molecular beam epitaxy (MBE) and show that a broad range of experimental results can be understood in terms of a few basic processes at the atomic scale. A continuum growth equation is derived from the underlying atomistic processes, thereby creating a complete mathematical model of the surface morphological dynamics of GaAs during growth, at micron and sub-micron length scales. The model accurately describes the rather complex surface shapes that are observed in re-growth on low-slope patterned GaAs surfaces. It is anticipated that this analysis will be applicable more generally to other materials including, especially, other compound semiconductors.

In this review, we begin with a summary of the experimental measurements of GaAs surface morphology, including in-situ measurements during MBE growth using elastic light scattering as well as ex-situ light scattering and atomic force microscopy (AFM) measurements. For more details on the measurements described below, the reader is advised to refer to the original references. Following the discussion of the experimental results, we present a mathematical derivation of the continuum growth equation that describes these results. The model is based on the atomistic dynamics in the Burton-Cabrera-Frank picture of crystal growth [1]. The derivation of the continuum equation from the atomistic processes is not exact and involves certain plausible, but difficult-to-quantify, assumptions. Therefore, we test the continuum analysis by comparing it with kinetic Monte Carlo simulations in which the underlying atomistic processes are completely specified. Once we have confirmed the accuracy of the approximate continuum limit of the atomistic model, we can apply it with confidence to real systems, knowing that it will describe the continuum limit correctly if the atomic scale physical processes are the same. In our comparisons between theory and experiment, we

emphasize a quantitative comparison of simulated surface shapes and power spectral densities rather than relying solely on matching scaling exponents.

This review brings together a number of disparate experimental results on GaAs surface morphology into a common theoretical framework for the first time. We also include several new interpretations of earlier experimental results that were not well understood at the time of the original work. The new interpretations are based on insights gained from subsequent work.

## **2. Measurements of Surface Morphology**

The characteristic surface roughness which develops during the thermal desorption of the native oxide from the surface of GaAs in ultrahigh vacuum provides a convenient random initial condition for studies of surface shape evolution. Although the native surface oxide can be removed from GaAs in a variety of ways, the most common and easiest method is to thermally evaporate it by ramping the substrate temperature up to  $\sim 600^\circ\text{C}$  [2]. The oxide comes off in two steps during the temperature ramp. First, the As oxide evaporates continuously in a layer-by-layer manner at  $\sim 400^\circ\text{C}$ . This is followed by the explosive evaporation of the Ga oxide, typically above about  $600^\circ\text{C}$  depending on the oxide thickness, which creates a pitted surface as shown in Fig. 1 [3]. A plausible explanation for this interesting phenomenon is that the surface  $\text{Ga}_2\text{O}_3$  layer reacts exothermically with Ga below the surface to form volatile  $\text{Ga}_2\text{O}$ . This picture is supported by the appearance of  $\text{Ga}_2\text{O}$  in the residual gas in the vacuum chamber during the oxide desorption. When the oxide is gone, the surface morphology consists of randomly dispersed 10-30 nm deep pits separated by 500-1000 nm as shown in the first panel in Fig. 1. If the polished substrate is illuminated with an intense light, the oxide desorption can be observed by eye as the appearance of a faint haze on the surface [3]. This roughening during the oxide desorption was either ignored or not recognized by early GaAs MBE growers, although it is standard practice to grow a buffer layer several hundred nanometers thick first, before depositing the layers of interest. The buffer layer acts to smooth the surface roughness produced by the thermal oxide desorption. Since the first step in epitaxial growth typically involves roughening the surface during the oxide removal followed by smoothing it with a buffer layer, the common practice of using highly polished, atomically flat substrates is most likely unnecessary if the oxide will be removed thermally.

There are at least two other methods for removing the surface oxide that do not cause the surface pitting that takes place in the thermal cleaning process. Atomic hydrogen exposure is

one example [4-8]. Atomic hydrogen is most easily produced by cracking  $H_2$  with a hot tungsten filament in front of the substrate. The hydrogen cleaning is efficient in the sense that close to 100% of the H atoms that strike the surface react with the oxide, and contribute to the oxide removal. The hydrogen cleaning also removes carbon, although not as efficiently as in the case of the oxide [4]. The atomic hydrogen does not remove silicon dioxide [4] which seems to be invariably present on the surface in trace amounts. Although there is no large-scale roughness analogous to the roughness produced by the thermal oxide removal, there is evidence of short length scale roughening [9] associated with hydrogen cleaning. Yet another way to remove the oxide is by exposure of the surface to a Ga beam [10-12]. In this case, care must be taken to avoid too much Ga exposure and nucleation of Ga droplets.

After depositing a few hundred nanometers of buffer layer on a thermally cleaned surface at a typical growth temperature of 550-580°C, the pitted surface tends to fill in leaving shallow mounds with the same spacing as the original pits. The mounds have characteristic rounded tops and V-shaped valleys. An example of one of these surface mounds is shown in Fig. 2. Cho studied the surface morphology of GaAs with electron microscopy using Pt shadowed carbon replicas, before the development of scanned probe microscopy. He showed that the thermally cleaned surface was rough and that the roughness was reduced after deposition of 15 nm of GaAs, and practically gone after 1  $\mu\text{m}$  of material had been deposited [13]. No doubt unaware of this work, Johnson, Orme and collaborators, in a series of highly cited papers, interpreted scanning tunneling microscope measurements of the mounds, as evidence that GaAs growth is unstable [14-16]. In this context, unstable growth means that surface mounds form spontaneously even on a flat starting surface due to a tendency of adatoms to migrate uphill, caused for example, by the Ehrlich-Schwoebel (ES) effect, and leading to a monotonically increasing surface roughness with time. The ES effect is a consequence of the asymmetric potential barriers that can be present at step edges and which tend to block the transfer of adatoms from upper terraces to lower terraces by diffusion over a step edge. This effect is well documented in the case of metals (see for example [17,18]). Smilauer and Vvedensky [19] used a potential barrier at step edges that inhibited interlayer transport in a kinetic Monte Carlo simulation of the oscillations in the intensity of electron diffraction spots during GaAs growth, and the subsequent recovery of the diffracted intensity when the growth was interrupted. However these authors acknowledge that step edge barriers would cause roughness to develop

during growth, which was not observed. They concluded that there must be a competing mechanism (eg “downhill funneling”) by which the deposited adatoms tend to smooth the surface during growth [19]. The work by Johnson et al [14] was picked up in the theoretical literature as yet another example of a system that exhibits unstable growth and tended to further focus theoretical efforts on the problem of unstable growth. In the meantime, other experiments began to appear that showed that GaAs growth is actually stable [20-23], consistent with the practical experience of people involved in semiconductor device fabrication, who had no difficulty growing smooth interfaces in GaAs. Scanning tunneling microscope studies of surface morphology in MBE growth of another semiconductor material, Ge(100), show that the ES barrier is small ( $\sim kT$ ) or non-existent for this system [24,25].

A graphic demonstration that GaAs growth is stable is presented in the atomic force microscope images in Fig. 1b-d of the surface of a series of progressively thicker GaAs buffer layers. These figures demonstrate that the amplitude of the surface roughness decreases with the thickness of the deposited layer. The surface mounds associated with regrowth on the rough thermally de-oxidized substrate are clearly visible in this figure. In Fig. 3 we show a similar decrease in surface roughness measured by elastic light scattering during growth. The large increase in scattered light intensity at 25 minutes in Fig. 3 is due to the roughening that takes place during the oxide desorption as the sample temperature is ramped up. There is a surface smoothing while the substrate is held at 620°C in an As<sub>2</sub> flux with the Ga shutter closed, which slows down as the substrate temperature drops to the growth temperature, as shown in Fig. 3a. When the Ga shutter is opened and GaAs growth begins, the surface starts to smooth rapidly. The background light scattering before the oxide roughening takes place in Fig. 3 is due to particles or other point defects on the growth surface or scattering of the specularly reflected laser beam inside the growth chamber. Numerous particles are typically visible on the surface after growth and in fact in the early days it was unclear whether or not the changing light scattering signal during growth was an intrinsic effect associated with the epitaxial growth, or an extrinsic effect associated with surface particles.

The possibility that diffuse light scattering is due to particles was ruled out in an elegant experiment by Pinnington [26-28] who used the light scattering from the 1D crosshatch pattern in a relaxed InGaAs layer as a reference to isolate the scattering by surface particles from the scattering by the random 2D surface roughness. This was done as follows: in relaxed

InGaAs/GaAs, the interfacial misfit dislocations produce orthogonal arrays of ridges on the surface along the  $[110]$  and  $[1\bar{1}0]$  directions as the deposited InGaAs migrates in response to the strain field of the misfit dislocation lines at the substrate interface. The light scattering from the linear arrays of randomly spaced 1D ridges on the surface is one-dimensional and clearly distinct from the scattering from particles, which is isotropic. In fact, a laser beam at normal incidence to the crosshatch patterned surface back-scatters into two orthogonal sheets of scattering, which make a bright cross on a screen that is placed to intercept the back-scattered light. By comparing the 1D and 2D light scattering with the power spectral density obtained from atomic force microscope (AFM) images of the surface of these samples, Pinnington was able to show that the intensity of the isotropic scattering is consistent with the observed 2D surface roughness, and therefore is not dominated by particle contamination. Since the random 2D roughness on the relaxed InGaAs layers is similar in amplitude to the surface roughness measured in other samples without the surface crosshatch pattern, we can conclude that the light scattering is indeed measuring the surface morphology.

In some thermally cleaned samples, the light scattering signal does not decay monotonically when growth is initiated, but rather first decays and then increases, sometimes far above the scattering associated with the thermal pits, before eventually decreasing again, as shown in Fig. 4 [4]. This phenomenon is believed to be due to islands of surface contaminants, such as carbon or  $\text{SiO}_2$ , which the deposited GaAs does not wet. During the initial stages of film growth, a non-wetting region will accentuate the surface roughness, before eventually being buried when the film is thick enough.

The power spectral density of the surface morphology can be determined by Fourier transforming AFM images [27] or by measuring the angular dependence of the intensity of the scattered light [29]. The power spectral density of regrown, thermally deoxidized GaAs surfaces obtained from AFM images is shown in Fig. 5 [23,30]. A somewhat larger spatial frequency range extending to lower frequencies can be obtained from light scattering measurements, although the spatial frequency range of AFM and light scattering overlap [29]. During growth, only a few discrete scattering angles corresponding to optical access ports in the growth chamber are readily accessible, whereas after the sample is removed from the vacuum chamber the scattering can be measured over a continuous range of angles. The scattered light intensity,  $I$ , is proportional to the power spectral density according to the following expression [31],

$$\frac{dI}{Id\Omega} = \frac{16\pi^2}{\lambda^4} \cos \theta_i \cos^2 \theta_s Q(\theta_i, \theta_s) g(q) \quad [1]$$

where the scattering is measured as a function of angle in the plane of incidence. In this equation,  $\theta_i$  is the angle of the incident light,  $\theta_s$  is the angle of the scattered light,  $Q(\theta_i, \theta_s)$  is a polarization dependent Fresnel factor, and  $g(q)$  is the power spectral density of the surface morphology as a function of spatial frequency  $q = 2\pi(\sin \theta_i - \sin \theta_s)/\lambda$ , which can be regarded as the “in-plane momentum transfer” that conserves the photon momentum in the elastic light scattering process.

The power spectral density derived from light scattering outside the growth chamber is shown in Fig. 6. Both the light scattering and the AFM show a broad peak in the power spectral density at  $q \sim 5 \mu\text{m}^{-1}$  with an amplitude of  $\sim 10^7 \text{ nm}^4$ . This spatial frequency corresponds approximately to the average spacing of the pits formed in the thermal oxide desorption in Fig. 1. During growth of the buffer layer, the power spectral density decreases for  $q > 2 \mu\text{m}^{-1}$  due to smoothing of the pitted surface, and increases for  $q < 2 \mu\text{m}^{-1}$ , presumably due to kinetic roughening. After a thick layer has been deposited, the characteristic length for the surface morphology disappears, replaced by a scale invariant power spectral density with asymptotic  $q^{-2}$  dependence as shown in Fig. 7 [29]. The  $-2$  power law for the spatial frequency dependence of the power spectral density is characteristic of kinetic roughening according to the Edwards-Wilkinson (EW) equation with non-conservative noise [32,33],

$$\partial_t h = F + \nu \nabla^2 h + \delta F \quad [2]$$

where  $F$  (nm/s) is the growth rate,  $\delta F \sim F$  is shot noise in the adatom arrival rate from the vapor and  $\nu > 0$  is a growth parameter which describes the rate at which surface features are smoothed out.

The EW equation (Eq. 2) can be solved in the Fourier domain for the power spectral density [33] when the noise term corresponds to white, and spatially uncorrelated, flux noise. The random noise acts as a driving term and produces the power spectral density,

$$g(q) = F \frac{1 - \exp(-2\nu q^2 t)}{\nu q^2}. \quad [3]$$

Kinetic roughening is caused by noise associated with the non-equilibrium growth process, for example the random arrival of deposited adatoms. This causes an initially flat surface to roughen

during growth. In the case of unstable growth the atomic scale randomness is amplified by the instability in the growth. The roughening effect is largest at low spatial frequencies as indicated by Eq. 3. It is difficult to observe kinetic roughening during growth on a thermally cleaned GaAs substrate, except at low spatial frequencies ( $q < 1 \mu\text{m}^{-1}$ ), since the surface is rough to start with and the main effect of the growth is to smooth the surface. The kinetic roughening can be more easily observed with growth on a smooth atomic-hydrogen cleaned surface. Atomic hydrogen cleaning does not produce the peak in the power spectral density near  $5 \mu\text{m}^{-1}$  that is observed with thermal de-oxidation [9,34], although there is some roughening at high spatial frequencies ( $q > 10 \mu\text{m}^{-1}$ ) which smoothes during growth [9]. In the hydrogen-cleaned substrates, the surface roughness is found to increase during growth for  $q < 10 \mu\text{m}^{-1}$ . This can be observed with light scattering as shown in Fig. 7 [9,34]. From fits to the time dependence of the light scattering data in Fig. 8 using Eq. 3, we find  $\nu = 5.7$  and  $6.2 \text{ nm}^2/\text{s}$  in the  $[110]$  and  $[1\bar{1}0]$  directions, respectively.

The asymptotic power law form of the spectral density with exponent minus two in Fig. 7 is consistent with the linear EW equation, however the fact that the surface mounds in Figs. 1 and 2 lack inversion symmetry means that the growth equation must also contain a nonlinear term. Two well-known non-linear growth equations that satisfy the necessary symmetry requirements are the Kardar-Parisi-Zhang (KPZ) equation [33-36],

$$\partial_t h = F + \nu \nabla^2 h + \frac{\lambda}{2} (\nabla h)^2 + \delta F, \quad [4]$$

and the higher order equation MBE equation [37],

$$\partial_t h = F - \kappa \nabla^4 h - \lambda_2 \nabla^2 (\nabla h)^2 + \delta F \quad [5]$$

We note that the same growth equations can be used to describe surface morphology during chlorine etching of GaAs, in which case  $F$  is negative [8]. In the KPZ equation (Eq. 4), the nonlinear term is always positive (for  $\lambda > 0$ ) and therefore it is non-conservative in the sense that the average growth rate depends on the amplitude of the surface topography. This is inconsistent with the usual situation in MBE growth in which there is no significant re-evaporation and the growth rate is controlled entirely by the incident atom flux and not by the surface shape. The KPZ non-linearity is typically associated with a growth process in which the surface expands uniformly along the normal to the local surface. The non-linear term reflects the fact that the

growth rate projected on the normal to the average surface will be higher for sloping parts of the surface [36]. The higher order nonlinear term in Eq. 5 on the other hand is conservative, with average value equal to zero. In this case, the growth rate is independent of surface shape, consistent with usual MBE growth conditions. The scaling behaviors of the solutions of both equations have been studied in detail and differ from the behavior for the EW equation. For example, in KPZ the exponent that describes the  $q$ -dependence of the power spectral density is  $2(1+\alpha) = 2.77$  rather than 2 as in EW with nonconservative flux noise, where  $\alpha$  is the scaling exponent that relates the interface width to the lateral size of the surface[36]. In the case of the MBE equation with non-conservative noise, the exponent is 3.33, and with conservative noise the exponent is 2 [36]. In the low amplitude limit in the KPZ equation for which  $h < \nu/\lambda$ , the nonlinear term can be neglected and the EW behavior dominates.

In addition to equations for which both terms have the same order in the spatial derivatives, a real system might also be described by the mixed order equation,

$$\partial_t h = F + \nu \nabla^2 h - \lambda_2 \nabla^2 (\nabla h)^2 + \delta F . \quad [6]$$

In this equation, the nonlinear term is higher order (4<sup>th</sup> order) in the spatial derivatives than the linear term and can be neglected in the long time, long wavelength length. The fourth order term is irrelevant if the system is scaled to large length scales. However, for real systems in which measurements are made over a limited spatial frequency range set by experimental constraints, a mixed order equation can be appropriate. Also, short length and time scale phenomena that occur immediately after growth commences are also of interest [38,39]. Ultimately, the experimental values of the coefficients will determine whether the conservative nonlinear term is important in the length and time regime of the experiments.

In order to compare the experimental results with the continuum models, we simulate the surface shape evolution by solving the KPZ equation numerically, neglecting for the moment the fact that the equation is not conservative and therefore physically inconsistent with the conservative nature of typical MBE experiments. An experimental AFM image of a thermally de-oxidized surface is used as the initial condition and  $\nu$ ,  $\lambda$  in Eq. 4 are used as fitting parameters. The simulated surface topography is shown in the lower panel in Fig. 1 next to the AFM images for the same growth times with  $\nu_x=10$ ,  $\nu_y=1$  nm<sup>2</sup>/s, and  $\lambda=12$  nm/s [23]. These values of  $\nu_x$ ,  $\nu_y$  are consistent with the values for  $\nu$  obtained from the time dependence of the

kinetic roughening measured with light scattering in Fig. 8. Visually, the simulations in Fig. 1 are in reasonable agreement with the data, although the simulation does not reproduce the anisotropy very well. A comparison of the power spectral densities for the AFM images and the simulations is shown in Fig. 5. There is good agreement between experiment and the KPZ equation. We conclude that the KPZ equation provides a good description of the experimental data for the range of growth times and spatial frequencies available in the experiments [22,23]. For the relatively low amplitude surface topography in these experiments, the linear term is more important than the nonlinear term in determining the surface dynamics; therefore the experimental data does not provide a particularly rigorous test of the nonlinear part of the growth equation. In fact, we find that the mixed-order equation also does a good job of describing the experimental data, as shown in Fig. 9 where we have simulated the same power spectral density data with Eq. 6 [40]. The two different nonlinear terms show comparable quality fits to the power spectral density data because the nonlinear term is relatively small compared to the nonlinear term over the power spectral density range of interest. We conclude that the experimental data does not cover a wide enough range of spatial frequencies to distinguish the second order nonlinear term from the fourth order one.

It has been suggested that a non-conservative KPZ-type nonlinearity could be present in the case of MBE growth if the adatoms had a sufficiently long diffusion length that they can be considered to form a 2D vapor on the surface [22]. In this case, adatom incorporation into the surface would mimic a chemical vapor deposition process, in which incorporation occurs in proportion to the exposed local surface area, and generate a KPZ-type nonlinearity. This purely geometrical explanation for the nonlinear term would give  $\lambda = F/2 \sim 0.1$  nm/s which is two orders of magnitude smaller than the experimental value,  $\lambda=12$  nm/s [23]. However, the mixed order equation (Eq. 6) with the conservative nonlinear term provides a more natural description, with a larger nonlinearity in agreement with experimental data, as we discuss below.

The magnitude of the asymptotic  $q^{-2}$  dependence of the power spectral density depends on the amplitude of the noise in the KPZ equation. In order to match the experimental data, it is necessary to increase the noise in the simulations by more than an order of magnitude above the shot noise in the deposition flux [23]. The physical origin of the excess noise during growth is not known and remains an outstanding problem. Clearly there are other random processes involved in the crystal growth in addition to the random arrival rate of adatoms which could

contribute to the kinetic roughening, including for example the random nucleation of new islands, and adatom attachment and detachment at step edges [18].

The most important results of the experiments on GaAs can be summarized by the following points. Initially rough surfaces become smooth during growth indicating that the growth is stable. The evolution of the surface morphology and the power spectral density with time are consistent with the KPZ equation and the conservative mixed order equation, both of which have a stable Edwards-Wilkinson-like linear term. Only the conservative equation is physically consistent with the experiments in which the growth rate is set entirely by the atom flux, in the absence of re-evaporation of adatoms. The surface-smoothing rate increases dramatically when growth is initiated indicating that the coefficients in the growth equation depend on the flux of deposited adatoms. In the next section, we show how all of these experimental results can be explained in terms of an adatom transport model derived from a few basic atomistic processes.

### **3. Atomistic Basis for Continuum Growth Equations**

#### **(a) Step Edges and Adatom Transport**

Epitaxial growth typically occurs through attachment of vapor deposited adatoms to step edges on the surface of a single crystal substrate, as shown schematically in Fig. 10. In the case of a locally flat surface (singular surface) the first stage of crystal growth involves the nucleation of monolayer islands. If the surface is misoriented with respect to a low index crystal plane (vicinal surface) or if there is initial surface topography, adatom incorporation will occur at pre-existing step edges, which will as a result tend to flow across the surface as the adatoms are incorporated.

Due to the asymmetric atomic structure in the vicinity of an atomic step, an adatom at the top edge of a step will in general experience a different potential barrier when hopping to a lower terrace (interlayer transport) than it experiences hopping on a flat terrace as illustrated in Fig. 10. The modified potential barrier at the step edge can modify the rate of hopping to the lower terrace so that it is either larger or smaller than the hopping rate on a flat terrace, thereby causing a net flux of adatoms either down- or up-slope. This effect is widely known in the literature as the Ehrlich-Schwoebel (ES) effect [41,42]. The ES effect has a striking impact on the shape of the grown surface, depending on whether the downward hopping rate is increased or decreased with respect to the flat terrace hopping rate. If the downward hopping rate is decreased the

growth becomes unstable, eventually leading to the formation of mounds. The step edge barrier also affects the reverse process, namely the hopping probability for an atom bound to a step edge back onto the upper terrace. In the case of a positive ES barrier, such as is shown in Fig. 11, adatoms bound to a step edge are more likely to be released out onto the lower terrace, than back to the upper terrace.

A site on the lower terrace close to a rising step has a similar asymmetry in the local atomic structure to the site above the step edge. This asymmetry can modify the energy barrier for adatom incorporation into the step edge, in the same way that the ES effect modifies the adatom diffusion over the top of the step edge. A repulsive potential close to an uphill step will tend to generate a downhill flux similar to a negative ES barrier [43]. A positive (repulsive) incorporation barrier is also known as an inverse ES barrier [44,45]. Fig. 11 shows an example of attractive incorporation barrier ( $E_{inc}$ ) that favors uphill adatom migration. For semiconductors with the zincblende crystal structure in which the interatomic bonds are covalent and directional, the atomic structure and bonding in the vicinity of a step edge is relatively complex, and there is no way the sign of the ES and incorporation barriers can be guessed intuitively with the current state of knowledge. When there is both a positive ES barrier and a positive incorporation barrier, the largest barrier will dominate and determine whether the adatoms migrate uphill or downhill.

The ES effect was first observed in field ion microscope images of adatom diffusion on metal surfaces [41]. Metals remain the best-understood examples of systems with repulsive ES barriers that hinder adatom migration to lower terraces [17,18]. Although a potential barrier at surface step edges is one possible mechanism by which an adatom current can be generated that flows uphill or downhill on the surface, several other mechanisms are also possible. Rather than hopping over a step edge, an adatom on an upper terrace can insert behind a step edge atom and push the step edge atom into the next lattice site on the lower terrace [46]. Alternatively this insertion process can be enhanced by the arrival of energetic adatoms from the vapor, which “knock-out” the step edge atom [47]. In another mechanism, the hot incoming atom from the vapor is allowed to “search” a small region near its impact site, to maximize its coordination number in that vicinity (also referred to as “downhill funneling”) [48,49]. In yet another mechanism, a foreign atom on the surface (surfactant atom) can reduce the potential barrier to adatom transfer from an upper terrace to a lower terrace [50,51]. All of these processes tend to stabilize the surface during growth.

Other examples of destabilizing mechanisms in addition to the positive ES barrier also exist. For example, an incoming atom from the vapor will experience a lateral force as it approaches the surface in the vicinity of a step edge while it is still in the gas phase, due to the asymmetric nature of the attractive surface potential near a step edge [52-54]. This causes a net up-hill displacement of incoming atoms in the vapor phase; a lateral displacement of even one lattice site for incoming atoms close to step edges, is sufficient to produce a measurable effect. It is of course possible that there is a combination of factors at work in any given physical situation. Of all these different physical mechanisms for interlayer transport, the positive ES barrier is best supported by experimental and theoretical evidence.

It is worth noting that the ES barrier is only effective in generating a net flux of adatoms in the direction of the surface slope in the non-equilibrium situation in which there is a net flux of atoms onto the surface from the vapor phase. In thermal equilibrium, an asymmetric potential barrier will not cause any uphill or downhill bias in the diffusion of adatoms on the surface.

### **(b) Growth on an Amorphous Substrate**

Extensive experimentation has shown that elemental metals typically have positive ES barriers [17] and therefore commonly show unstable growth leading to surface mounds. We explore the alternate and simpler case of stable growth motivated by experimental data for epitaxial growth of GaAs(100). The shape of growing surfaces depends on the migration and attachment of adatoms on the surface. Therefore, the first step in describing the surface shape is to write down a transport equation for adatoms.

Before addressing the problem of single crystal growth we consider a simpler situation in which the surface is amorphous with randomly located attachment sites for adatoms. The adatoms are assumed to be free to diffuse on the surface until they find a randomly located attachment site. The reverse process is also allowed, namely adatoms can be thermally released from attachment sites. In this case, the surface transport equation is particularly simple [55]:

$$\partial_t n = \frac{G}{\sqrt{1+(\nabla h)^2}} - \frac{n}{\tau} + C + D\nabla_s^2 n. \quad [7]$$

In this equation  $h$  is the surface height measured with respect to a flat reference plane,  $n$  is the density of adatoms in units of atoms/nm<sup>2</sup>,  $G = F/a^3$  is the rate of adatom deposition from the vapor in units of atoms/nm<sup>2</sup>/s,  $C$  is the rate per unit area of thermal release of adatoms from attachment sites back into the mobile adatom phase,  $D$  is the diffusion coefficient of adatoms,

and  $\tau$  is the characteristic time required by an adatom diffusing on the surface to find an attachment site. In general, one would expect the adatom capture and release rates at attachment sites to depend on the deposition rate since the surface structure will be driven into a metastable configuration during steady state growth. Therefore  $\tau$  is the adatom lifetime at the particular deposition rate  $F$ . The gradient operator  $\nabla_s$  is taken with respect to a coordinate  $s$  that follows the local surface topography. In Eq.7 we assume that the temperature is low enough that thermal evaporation off the surface, back into the vapor phase, can be neglected. The adatoms are assumed to arrive at the surface ballistically in a parallel beam normal to the plane of the average surface. This means that for sloping parts of the surface, the local adatom flux density per unit surface area is smaller since the local surface area exposed to the vapor is larger by the factor  $\sqrt{1+(\nabla h)^2}$ .

The adatom incorporation and release from attachment sites on the surface drives changes in the surface height as follows [55]:

$$\partial_t h = a^3 \sqrt{1+(\nabla h)^2} \left( \frac{n}{\tau} - C \right). \quad [8]$$

For typical growth conditions, we expect the shape of the surface to evolve rather slowly compared to the rate at which individual adatoms hop on the surface. In this case, we can set  $\partial_t n \approx 0$  in Eq. 8. This ‘‘adiabatic’’ approximation is commonly used in the solution of coupled differential equations. We solve for  $n$  in Eq. 7 by Fourier transforming and keeping the lowest order in the derivative. This method is equivalent to applying the inverse operator,  $(1 - D\tau\nabla_s^2)^{-1} \approx 1 + D\tau\nabla_s^2$ , to solve Eq. 7 in the static limit [56]. The result is

$$n \approx G\tau + \frac{G\tau}{\sqrt{1+(\nabla h)^2}} - \frac{GD\tau^2}{2} \nabla^2 (\nabla h)^2 \quad [9]$$

which is valid in the limit of low surface slopes. To lowest order in the surface slope  $\nabla_s \approx \nabla$ , therefore we can drop the subscript  $s$  from the gradient operator. Substituting this expression for  $n$  into Eq. 8 gives the growth equation,

$$\partial_t h \approx F \left( 1 - \frac{D\tau}{2} \nabla^2 (\nabla h)^2 \right) \quad [10]$$

to lowest order in the surface gradient. This growth equation is conservative in the sense that the average growth rate is independent of the surface shape as required when the deposited atoms do not re-evaporate. The nonlinear term in the growth equation arises from a purely geometrical effect, namely that the adatom flux density is lower on sloping parts of the surface. Since the sloping parts of the surface receive a lower areal density of adatoms from the vapor than the locally horizontal parts of the surface, diffusion of adatoms from the high concentration regions to the low concentration regions causes a net flow of adatoms from horizontal parts of the surface to sloping parts. This is the physical mechanism underlying the nonlinear term in the growth equation. This argument for the conservative nonlinearity in Eqs. 5 and 6 can be compared with the geometrical argument for the non-conservative  $(\nabla h)^2$  term in the KPZ equation discussed above. The KPZ-type nonlinearity might be expected to take place in chemical vapor deposition at atmospheric pressure for example, but is less natural in MBE where the adatoms arrive ballistically in a directed beam without gas phase collisions.

Eq. 10 is an approximate growth equation since we have truncated an infinite series of higher order derivatives, keeping only the lowest order derivative. The infinite series of derivatives in the exact equation reflects the fact that the growth process is non-local. Because the adatoms diffuse on the surface, the growth rate at a given position depends not only on the local shape of the surface at that position but also on the shape of the surface everywhere else. In order to define the surface everywhere from its value at one point, one must know all the derivatives to infinite order.

Numerical solutions of Eq. 10 starting from random or patterned initial conditions produce parabolic mounds with rounded tops and V-shaped valleys. This kind of surface morphology is commonly observed in non-epitaxial thin films (eg. evaporated gold films on glass), although there may be other growth mechanisms which lead to a similar morphology. Eq. 10 describes the surface smoothing that takes place during physical vapor deposition in which the adatoms can diffuse on a solid surface. This rather elegant growth equation, which has a geometrical origin, may be more generally applicable in physical vapor deposition than the more commonly used Mullins equation [57,58], which is widely considered in the literature to be the appropriate growth equation in the presence of surface diffusion:

$$\partial_t h = F - \kappa \nabla^4 h + \delta F. \quad [11]$$

In the Mullins equation, the negative sign on the right hand side corresponds to stable growth. This linear equation is derived from a thermodynamic analysis in which surface adatom migration is driven by gradients in the surface chemical potential. The surface chemical potential is assumed to be proportional to the surface curvature, as in a liquid. As long as the chemical potential depends on the surface curvature, this equation should be applicable whether or not growth is taking place. However, Eq. 11 provides no insights as to how the metastable atomic scale surface structure that is present during deposition affects the chemical potential of the surface or how the parameter  $\kappa$  relates to atomistic processes that take place in crystal growth.

### (c) Epitaxial Growth on a Single Crystal Substrate

We now consider the case of epitaxial growth on a single crystal substrate. This is a problem of considerable practical importance as well as being an interesting scientific problem. In our analysis, we adopt an atomistic perspective, which we then extend to the continuum limit. For growth on a low index crystal face (a singular surface), growth occurs by nucleation of monolayer islands followed by attachment of adatoms to step edges as discussed above, and illustrated in Fig. 10. During growth on a singular surface, there will be an average step density  $S_0$  in steady state which will depend on the temperature and deposition rate. The step density is defined as the total length of the step edges divided by the area of the surface. This density turns out to be approximately equal to the reciprocal of the spacing between step edges and therefore it also defines a local surface slope. The random local slope associated with the growth-induced step density can be added quadratically to the macroscopic average surface slope to obtain the mean square slope [58,59],

$$S^2 = S_0^2 + \left(\frac{\nabla h}{a}\right)^2, \quad [12]$$

where  $a$  is the lattice constant. This expression serves to interpolate the step density from a zero average slope surface with random steps to a high slope surface that approximates a stairway. The interpolation formula will be correct if the random slope is uncorrelated with the macroscopic average surface slope.

The presence of ES barriers at step edges leads to a diffusion bias, which causes the adatoms to drift up or down the macroscopic average slope on the surface [60]. The net adatom current on the surface due to the diffusion bias is easily determined from the solution of the 1D

diffusion equation. The one dimensional diffusion equation on a terrace bounded by two parallel steps at  $x=[0,L]$  is,

$$D\partial_x^2 n + G = 0 \quad [13]$$

where  $D$  is the diffusion constant of the adatoms and  $n$  is the density of adatoms. In one dimension, the solution is

$$n = -(G/2D)x^2 + Ax + B \quad [14]$$

where A, B are constants determined by the boundary conditions. The boundary conditions at the step edges at  $x=[0,L]$  are as follows,

$$\begin{aligned} D\partial_x n|_{x=0} &= v_0 n|_{x=0} - C_0 \\ D\partial_x n|_{x=L} &= -v_L n|_{x=L} + C_L \end{aligned} \quad [15]$$

were  $C_0$  and  $C_L$  are the rate at which adatoms are released from the step edges onto the terrace at  $x=0$  and  $x=L$  respectively. The coefficients  $v_0, v_L$  are capture velocities which are proportional to adatom hop rates into the step edge. The net rate of change of adatom density is the deposition rate minus the net capture rate at the step edges which form the borders of the terrace. The net capture rate is equal to the sum of the particle currents into the boundaries at  $x=0$  and  $L$ . Neglecting the difference between  $v_L, v_0$  ( $v_0 = v_L = v$ ) and  $C_L, C_0$  ( $C_L = C_0 = C$ ), and further assuming that  $vL \gg D$ , we find from the solution of the diffusion equation that the net generation/capture rate for adatoms is

$$\partial_t \langle n \rangle = G - 12(D\langle n \rangle - aC)/L^2, \quad [16]$$

where  $\langle n \rangle$  is the average adatom density on the terrace. In this expression, we have also used  $D = av$ , which is derived in the Appendix. The important feature of this result is that the capture and release rates of adatoms from the step edges in Eq. 16 are inversely proportional to the square of the terrace width. This dependence is expected to be independent of the shape of the step edges. On the other hand, the numerical constant (12 in Eq. 16) results from our assumption of straight-parallel steps and will be sensitive to the shape of the step edges, for example whether they are parallel lines or circular loops.

The net diffusion current on the growing surface is equal to the difference in the flux of adatoms at the two step edges,

$$J_L = -D[\partial_x n|_{x=0} + \partial_x n|_{x=L}], \quad [17]$$

where we assume that the step at  $x=0$  is an uphill step and the step at  $x=L$  is a downhill step with positive adatom current in the direction of increasing  $x$ . In the case of a positive ES barrier, a characteristic length  $\ell_{es} = D/v_L$  known as the Ehrlich-Schwoebel length can be defined [58]. Solving the diffusion equation subject to the slope boundary conditions in Eq. 15 we find the following expression for the adatom current density in Eq. 17,

$$J_L = \frac{D[GL(v_L - v_0) + (C_0 v_L - C_L v_0)]}{(v_0 D + v_0 v_L L + v_L D)}. \quad [18]$$

The ES potential at the step edge, illustrated in Fig. 11, affects both the adatom release rate from step edges as well as the rate of hopping from upper terraces to lower terraces. Although hopping from the lower terrace to the upper terrace will be slow compared to the reverse process, since the atom on the lower terrace must break a lateral bond to the step edge, the barrier lowering (negative ES barrier) will increase the rate of hopping-up by exactly the same factor that it modifies the hopping-down rate for an adatom located immediately above the step edge. Therefore, we expect  $C_0/C_L = v_0/v_L$ . This ensures that the principle of detailed balance is obeyed in Eq. 18, namely that in thermal equilibrium when  $G=0$  there is no net adatom flux associated with the ES barrier.

In earlier papers by the present authors [59,61], this principle was overlooked and the directionality in the step edge release rate associated with the ES barrier was neglected. This has the effect of overestimating the smoothing effect associated with negative ES barriers by neglecting a competing up-hill flux associated with adatom release from step edges.

In this review, we are primarily interested in dynamics of surfaces with low slopes close in angle to a low index crystal plane. If the macroscopic average surface slope is small ( $\nabla h \ll a/L$ ) there will be several up-down step pairs (ie monolayer islands) between each net downward step. Only the net downhill steps will contribute to the diffusion bias. In this case the slope-related current is reduced in proportion to the fraction of net downhill steps:

$$J = J_L \frac{L}{a} \nabla h = \frac{DGL^2(v_L - v_0)}{a(v_0 D + v_0 v_L L + v_L D)} \nabla h. \quad [19]$$

Since  $v_L, v_0 \gg D/L$ , we can simplify this expression as follows,

$$J \approx \frac{\xi G}{S} \nabla h \quad [20]$$

where the Ehrlich-Schwoebel parameter  $\zeta$  is defined as

$$\zeta = \frac{D}{a} \left( \frac{1}{v_0} - \frac{1}{v_L} \right). \quad [21]$$

In this and subsequent equations, we replace the terrace width  $L$  by  $1/S$ , the average step density. Physically this expression for the downhill ES current is very simple. It consists of the product of three quantities: (i)  $\zeta$ , the expectation value for a net downhill motion by an adatom on top of a step edge, (ii)  $Ga$ , the number of particles deposited per unit length along a single row of atoms on the crystal surface and (iii)  $\nabla h/aS$ , the fraction of the terraces that are vicinal and are therefore capable of generating a net downhill diffusion flux. This expression is remarkably robust in that it will have the same form for most of the step edge mediated smoothing mechanisms including downhill funneling, step edge insertion, incorporation barriers at the uphill steps etc.

We can now write down an adatom transport equation from the requirement that the adatom density be conserved,

$$\partial_t n = G + \frac{\zeta G}{S} \nabla^2 h + D \nabla^2 n + \beta a C S^2 - \beta D S^2 n, \quad [22]$$

where  $\beta$  is a numerical constant that depends on the shape of the step edges. In the case of straight parallel steps,  $\beta=12$  as discussed above. In the continuity equation, we have neglected terms of third and higher order in  $h$  when taking derivatives. Since all adatom transport takes place on terraces, which are assumed to be oriented parallel to the macroscopic average surface, there is no need to include derivatives in the plane of the local average surface, as in Eq. 7 above.

In Eq. 22, we have neglected the nucleation of new monolayer islands. Since nucleation creates new step edges, it would be necessary to include nucleation if we wished to describe the time dependence of the step density, which would require a rate equation for the step density in addition to the adatom rate equation, and coupled to it. Neglecting nucleation is consistent with assuming a constant steady-state step density. The filling-in of monolayer holes and creation of new islands by nucleation is implicitly assumed to be going on continuously so as to maintain a constant average step density. For a singular surface (zero average slope), the step spacing in steady state will be equal to the maximum distance an adatom can diffuse before encountering other adatoms and nucleating a new island. Therefore the zero slope step density in Eq. 12 is

related to the adatom diffusion length according to  $S_0 \sim \ell_D^{-1}$ , where  $\ell_D$  is the diffusion length [58].

The adatom transport equation is similar to the transport equation for minority carriers in semiconductor devices, where the adatoms play the role of electrons and the step edges act as recombination centers. The surface slope is analogous to an electric field, which drives the surface current of adatoms, and the flux of atoms from the vapor is analogous to the generation of minority carriers with light; each adatom attachment event at a step edge corresponds to an electron-hole recombination event. Unlike the minority carrier drift/diffusion equation where recombination causes free carriers to vanish without a trace, in the adatom transport process each “recombination” event leaves a mark by increasing the surface height.

For typical experimental conditions in crystal growth, the adatom dynamics are fast compared to the rate at which the surface shape changes. In this case, we can make the adiabatic approximation discussed above and set  $\partial_t n \approx 0$  in Eq. 22. This equation can be solved for  $n$  using the Fourier transform method discussed above.

$$n = \frac{\zeta G}{\beta D S^3} \nabla^2 h + \frac{G + \beta a C S^2}{(\beta D S^2 - D \nabla^2)} \quad [23]$$

$$\approx \frac{1}{\beta D S_0^2} \left[ \frac{\zeta G}{S_0} \nabla^2 h + (G + \beta a C S_0^2) - \frac{G \nabla^2 (\nabla h)^2}{\beta a^2 S_0^4} \right]$$

In this expression, we have kept the lowest order linear and nonlinear terms in  $h$ . The higher order nonlinear terms can be neglected in the limit that the surface slope is small or  $\nabla h < a S_0$ . In the case of the term linear in  $h$  we have kept only the first term in the infinite series:

$\nabla^2 h + (\beta S_0^2)^{-1} \nabla^4 h + (\beta S_0^2)^{-2} \nabla^6 h + \dots$ . This approximation is valid in the limit that the

wavelength of the surface undulations  $\lambda$  is large or  $\lambda > 2\pi / (\sqrt{\beta} S_0)$ . Alternating terms in this

series beginning with the  $\nabla^4 h$  term are unstable, in that they amplify small oscillations in the surface (“antidiffusion”). We are justified in truncating the unstable terms because the series is stable when summed to infinity. In Eq. 23 we have expanded the expression for the step density in step density to lowest order in the surface slope as follows: The film growth rate is defined by the net rate at which adatoms are captured at step edges as follows,

$$\partial_t h = \beta a^3 (D n S^2 - a C S^2). \quad [24]$$

We substitute the expression for  $n$  from Eq. 23 into Eq. 24 and obtain the remarkably simple growth equation,

$$\partial_t h = F + \frac{\zeta F}{S_0} \nabla^2 h - \frac{F}{\beta a^2 S_0^4} \nabla^2 (\nabla h)^2, \quad [25]$$

where we define the growth rate  $F$  as a velocity  $F = Ga^3$ . This is a conservative nonlinear growth equation of mixed order in the spatial derivatives. It represents a formal derivation of the continuum growth equation in Eq. 6 and illustrates a general approach to deriving equations for surface dynamics from surface particle transport. In the large length scale limit (small spatial frequencies), the nonlinear term is irrelevant in the sense of scaling. However, experiments cannot be arbitrarily scaled to large lengths, and this term turns out to be important in the interpretation of experimental data for GaAs. The dependence of the coefficient of the nonlinear term on  $F$  and  $S_0$  in Eq. 25 was derived by Politi et al. using dimensional analysis [62]. The random nucleation of islands tends to smooth out sharp features and creates a fourth order smoothing term  $-\kappa \nabla^4 h$  with  $\kappa \sim (F/aS_0^4)$ . Politi and Villain inferred this result from numerical solutions of the equations for step motion in the presence of a positive ES barrier [62], and obtained the coefficient  $\kappa$  by dimensional analysis (see also references [58, 63, 64]). The higher order linear term is helpful, even essential, as a regularization term that stabilizes the numerical solutions of Eqs. 10 and 25. The coefficient of the linear term in Eq. 25 reproduces the results of Vvedensky [65] if the constraints of the Wolf-Villain model [66] are applied, namely that the adatom moves immediately to the highest coordination nearest neighbor binding site when it lands on the surface.

It is interesting that the coefficients in the epitaxial growth equation in Eq. 25, that was derived from an adatom transport equation, does not depend on the adatom diffusion constant. Physically, one might expect the adatom mobility to be as important as the deposition rate in determining the growth parameters. Fundamentally, all surface shape changes are caused by the diffusion of adatoms on the surface. Although the growth equation does not depend on the diffusion coefficient directly, it does depend on it indirectly through its effect on the step density. A better intuitive picture of the physical significance of the nonlinear term can be obtained by considering the special case when the critical cluster size for nucleation of a new island consists of three atoms. In this case, the step density depends on the diffusion coefficient as

$S_0 \sim (G/D)^{1/4}$  [33]. Substituting this expression for  $S_0$  into the expressions for  $\nu$  and  $\lambda_2$  in Eq. 25 gives  $\nu \sim \zeta a^3 G^{3/4} D^{1/4}$  and  $\lambda_2 \sim aD$ . This value for  $\lambda_2$  is almost the same as the coefficient of the nonlinear term for growth on an amorphous substrate in Eq. 10 if we set the characteristic time for adatom incorporation into the film equal to time required to grow a monolayer. In this case  $\tau = a/F$  and  $\lambda_2 = FD\tau/2 = aD/2$  (from Eq. 10) which is equal, within a numerical constant, to the coefficient of the nonlinear term in Eq. 25. Therefore we can conclude that the coefficient of the nonlinear term in the equation for epitaxial crystal growth is closely related to the adatom diffusion constant.

Although we have so far not made any assumptions about the ES barriers or incorporation barriers at step edges, it is clear that in order to be consistent with the GaAs data, the net effect of these barriers must be to favor a downhill diffusion bias. Otherwise the growth would be unstable and an initially smooth surface would become rougher, contrary to experimental observations (see, for example, Fig. 1). However, we cannot tell from the experimental data whether the downhill diffusion bias is due to a negative ES effect, or to some other effect or combination of effects such as insertion of adatoms behind step edges, knockout, “downhill funneling” etc. Insertion behind a step edge can be regarded as a more complex form of negative ES barrier with different energetics. It is also possible that the ES barrier is positive but that the step edge incorporation barrier is larger and drives the downhill flux.

#### 4. Comparison with Kinetic Monte Carlo Simulations

Several important, but difficult to quantify assumptions are made in the derivation of the continuum growth equation. First, in the adatom transport equation, we have used results for diffusive capture of adatom at straight parallel steps, whereas in practice we know that the step edges will form random meandering lines on the surface. The adatom capture and release rates in Eq. 24 depend on the square of the step density. A random step pattern is unlikely to change this dependence but whether the step edges are parallel lines, or form convoluted patterns will certainly affect the dimensionless constant  $\beta$ . The second critical assumption is the quadratic form we have assumed for the step density as a function of surface slope (Eq. 12). Although there is no doubt that the step density will increase linearly with slope for large slopes as indicated by the assumed form in Eq. 12, for small slopes the situation is more complicated. In fact, as we show below, the step density may decrease with slope for small slopes, before

increasing again for large slopes [59]. It is difficult to quantify the effect of these, and other assumptions, on the accuracy of the continuum description that has been presented. Therefore, an independent test of the accuracy of the model is needed.

In principle, the model could be tested by comparing it with experiments, however in practice the atomic scale phenomena that take place in real systems are not well enough understood for experiments to be useful as a quantitative test. Instead, we test the continuum model by comparing it with kinetic Monte Carlo (kMC) simulations of a solid on solid model for epitaxial growth, restricted to eliminate double height steps [67-71]. In the kMC simulations, adatoms are deposited randomly on an  $N \times N$  square lattice with  $N = 300 - 1000$  atomic sites and periodic boundary conditions. The deposited surface atoms have bonds to up to four lateral neighbors. The deposition rate, the activation energy for adatom hopping on terraces, and the lateral binding energy for adatoms at step edges were chosen to be similar to values for GaAs(001) epitaxy estimated from experiments [72-75] and density functional theory [76,77]. In the simulations, the activation energy for hopping from one terrace site to another is chosen to be 1.25 eV and the lateral binding energy is 0.35 eV for each of up to four lateral bonds [59]. We don't know whether the diffusing species consists of a Ga atom alone or whether it is a Ga atom moving in concert with an As atom or atoms. In the kMC simulations the activation energy for hopping from an upper terrace to a lower terrace across a step edge is reduced by 0.05eV (ie  $E_{es} = -0.05$  eV) with respect to hopping on a flat terrace in order to simulate an ES barrier that favors downhill adatom migration. The ES barrier is difficult to calculate theoretically because the relevant binding energies must be determined with high accuracy, since even very small values in this parameter will have a strong effect on the surface shape [24]. In the simulations, the ES barrier was not included in the step edge release rate. Thus the probability of step edge atoms hopping to the upper terrace is the same as the rate of hopping away from the step edge onto the lower terrace [59]. This is not physically realistic since lowering the activation barrier to hopping down should also lower the barrier for the reverse process, namely hopping back up. Although the atomistic processes in the kMC simulation do not match a real system, nevertheless the kMC simulation still provides a test of the continuum model as long as the continuum model includes the same microscopic phenomena.

In Fig. 12, we show the evolving shape of an initially sinusoidal surface as a function of time for kMC simulation of growth on sinusoidal surfaces with two different spatial frequencies

and initial amplitudes. This figure shows that the nonlinearity in the surface growth, represented by the appearance of V-shaped valleys, increases with spatial frequency and the initial amplitude. The stronger nonlinearity for higher frequency surface patterns is qualitatively consistent with Eq. 25 where the nonlinear term has a higher order in the spatial derivative than the linear term. In the linear regime represented in Fig. 12a, the smoothing rate has an approximately quadratic dependence on spatial frequency as shown in Fig. 12d, consistent with the Laplacian term in Eq. 25.

The assumed expression for the step density as a function of surface slope in Eq. 12 is compared with the kMC simulations by imposing a constant slope as an initial condition on the solid on solid model. Once a steady state has been achieved under a constant adatom flux, the density of steps can be counted. At low surface slopes and high growth temperature, the density of surface steps oscillates with a period equal to the monolayer growth time. In this case, we compute the time average step density. The step density as a function of slope obtained in this way is shown in Fig. 13 for four different growth temperatures [59]. The simulation shows that at low growth temperature the surface step density is in good qualitative agreement with the assumed quadratic form (Eq. 12) as a function of surface slope, with a smooth monotonically increasing step density, becoming linear at large slopes. At high growth temperature, on the other hand, the step density is non-monotonic with slope, showing a minimum at a non-zero slope. The reason for this behavior is that for low slopes, the steps typically form closed loops surrounding monolayer islands or valleys (see Fig. 13b) while at higher slopes the steps tend to form parallel lines that extend across the sample perpendicular to the slope without closing on themselves (see Fig. 13d). It can be shown by solving the 2D diffusion equation numerically, that two-dimensional closed-loop steps characteristic of a singular surface are less efficient at capturing adatoms than the open, one-dimensional steps characteristic of a vicinal surface, for the same step density. The reason for this is that the straight parallel steps are all equally spaced and therefore maximally dispersed over the surface. In the case of circular step patterns, the step-step separation is not constant, which leads to a net reduction in capture rate for the same step density. The steady-state step density is defined by a balance between the rate of nucleation of new islands and the rate of filling in of previously formed islands. When the topology of the steps favors efficient capture of adatoms, the steady state step density will be lower since the density of adatoms and the nucleation rate will be lower for the same step density and atom flux.

In this case, the step density can in principle be lower at a non-zero slope than at zero slope. This effect goes away at low growth temperatures where the step edges are highly convoluted with many kinks. The distinction between linear steps and closed loop steps disappears when the step edges are highly convoluted, fractal-like, objects.

In order to determine the surface-smoothing rate in the kMC simulations, we start with an initially sinusoidal surface topography and allow the surface to smooth through deposition of adatoms. During the simulation, the amplitude of the topography decays while at the same time the shape of the initially sinusoidal surface distorts due to the nonlinearity in the growth process caused by lateral migration of adatoms. If the surface shape is properly described by Eq. 25 then the parameters in this equation can be determined by fitting the time dependence of the surface shape with Eq. 25, while treating the coefficients of the linear and non-linear terms as adjustable parameters. Since the kMC simulations allowed adatoms released from step edges to hop to the lower or upper terraces with equal probability ( $C_0 = C_L = C$  in Eq. 18), a modified version of the linear coefficient in Eq. 25 was used for the comparison with the numerical simulations. The modification consists of replacing  $\zeta F/S_0$  in the linear term in Eq. 25 with  $\zeta(F/S_0 + aC)$ . This has the effect of increasing the linear smoothing rate since the tendency of adatoms released from step edges to diffuse uphill is not included. In addition, the temperature dependence of the smoothing rate increases since the step edge release rate  $C$  is more strongly temperature dependent than the inverse step density  $1/S_0$ .

The comparison of the continuum model with the kMC simulation is accomplished by computing the first three Fourier coefficients of the numerical solution of the modified Eq. 25 as a function of time for a sinusoidal initial condition. The time dependence of these coefficients obtained from the numerical solution of the growth equation was matched to the time dependence of the first three Fourier coefficients of the kMC simulations using the coefficients in the growth equation as adjustable parameters. Typical fits to the surface shape using Eq. 25 are shown in Fig. 14 as a function of growth time. This figure also shows the first three Fourier coefficients in the kMC simulation and the corresponding coefficients for the continuum fit as a function of time. The  $\nu$ ,  $\lambda_2$  parameters in the continuum growth equation, which give the best fit, can be viewed as “experimental” values obtained from kMC “experiments”. Since all the parameters of the kMC model are known, in particular the step density and the flux, the theoretical values for the coefficients in the growth equation can be calculated from the

expressions for these coefficients in Eqn 25 and compared with the kMC “experiments” [59]. In Figs. 15a,b, we show the values for the coefficients  $\nu$ ,  $\lambda_2$  for the linear and nonlinear terms, respectively, in the growth equation as a function of flux and temperature obtained from fits to the “experimental” kMC simulations. Figs. 15a,b also show the values for  $\nu$ ,  $\lambda_2$  computed from the expression  $\nu = \zeta(F/S_0 + aC)$  as discussed above and  $\lambda_2 = F/a\beta S_0^4$  from Eq. 25, by substituting the appropriate atomistic parameters from the kMC simulations.

In this comparison, we have chosen  $\beta = 5$  as it gives the best match between the model and the kMC simulations. For straight parallel steps, a solution of the 1D diffusion equation similar to Eq. 16 shows that  $\beta = 12$  as discussed in connection with Eq. 16. For all other step configurations, adatom capture will be less efficient per unit step length and  $\beta$  will be smaller; therefore  $\beta = 5$  is reasonable. The shape of the step edges as well as the density of steps is a strong function of temperature. At high temperature, the step density is low and the step edges are relatively smooth. At low temperatures and high growth rates, the step density is high and the shape of the step edges is convoluted with numerous kinks and corners. Under these circumstances, one would expect  $\beta$  to be temperature and growth rate dependent. This is a fundamental limitation of the model, as we have no way of including the effect of complex step edge shapes. Changes in the shape of the step edges with temperature and flux may be responsible for the rather modest discrepancy between the kMC results and the continuum model in Fig. 15. Nevertheless, the continuum model does a remarkably good job of describing the temperature and flux dependence of the linear and nonlinear smoothing parameters in the kMC data, as shown in Fig. 15a,b.

A kMC simulation of growth on a surface with an initially trapezoidal shape is shown in Figs. 16 as a function of the thickness of the deposited layer. Also shown in this figure is the surface shape calculated from the continuum model in which the adatom transport equation and the surface height equation (Eqs. 22 and 24) are solved as a pair of coupled equations [61] with the various coefficients in the coupled equations treated as adjustable parameters. In these simulations, a step edge capture term of the form  $\beta DS_n/a$  was used rather than  $\beta DS^2n$  as in Eqs. 22 and 24. A step edge capture rate that is linear in the step density is appropriate if every surface site has an equal probability of being at a step edge. In reality, the step edges are in the form of “lines” on the surface and surface sites that are neighbors to step edge sites are more

likely to also be step edge sites. In this case, the quadratic dependence on step edge density is appropriate, as in Eqs. 22 and 24. Independent of whether the quadratic or linear dependence on step density is chosen for the step edge capture rate, there was little change in the surface shapes in the numerical solutions. Of course the magnitude of the step density required to match the data will be different.

The continuum model and the kMC simulation give very similar surface shapes, except that the kMC simulation shows additional structure near the top of the surface profiles. The kMC simulation has a ridge at the top center of the pattern and distinct shoulders on the edges of the ridges whereas the continuum model shows only a smoothly rounded convex top. The extra features in the kMC simulation are believed to be associated with the minimum in the step density as a function of surface slope illustrated in Fig. 13. This property of the step density is not part of the continuum model discussed here but is present in the kMC simulations.

## **5. Comparison with Experimental Data**

In this section, we compare the predictions of the continuum model with experimental data for surface shapes on GaAs(100) during MBE growth. Here, we ignore the fact that GaAs, being a compound semiconductor, necessarily requires the incorporation of two different atoms during growth whereas the models consider only a single species. In MBE growth of GaAs, the growth rate is controlled by the Ga flux and As is provided in excess. Therefore, in the comparison with the model, the experimental growth process can be regarded as effectively a single component system involving the migration and attachment of Ga atoms. Nevertheless there is still an additional variable namely the As overpressure, which is known to affect the diffusion rate of Ga [28,78]. In order to compare different experiments it is important not only to control the growth rate and substrate temperature, but also the As overpressure. The real system is further complicated by the presence of in-plane anisotropy and surface reconstructions [79], which are both affected by the As<sub>2</sub> or As<sub>4</sub> overpressure. The complexity of the system makes it difficult to calculate the surface potentials in the vicinity of step edges with the necessary accuracy to determine the ES coefficient in the growth equation.

The experiments clearly show that the surface smoothens with time; therefore, the growth is stable. Less obvious is whether there is a second order linear smoothing term (Edwards Wilkinson type) or a fourth order linear term as in the MBE equation (Eq. 5). Support for the second order linear term comes from the time evolution of the power spectral densities where the

second order term gives a better match to data [23]. In Fig. 18, we show the same power spectral density as in Fig. 5, together with a fit to the MBE equation with conservative noise [23].

Although the MBE equation with conservative noise reproduces the high spatial frequency part of the power spectral density rather well, including the  $-2$  slope at large  $q$ , it does not match the data at low spatial frequencies. The relative merits of the second order and fourth order linear terms are illustrated in a different way in Fig. 19(a) where we show line scans through a series of AFM images obtained for samples in which different thicknesses of GaAs have been deposited on thermally de-oxidized substrates [23]. This figure also shows simulations of the surface profiles using the KPZ, MBE and Edwards-Wilkinson equations. Starting from the bottom in Fig. 19(d), the scan lines for the Edwards-Wilkinson simulation quickly develop up-down symmetry as expected for a linear growth equation, but inconsistent with the experimental data in (a). In Fig. 19(c) the simulation with the MBE equation shows rapid smoothing of the high spatial frequency component in the scan lines, too rapid to be consistent with the data. The KPZ simulation in Fig. 19(b) gives the best match to the data with a good balance between the low and high spatial frequency smoothing as well as the V-shaped valleys. Although a simulation with the mixed order equation (Eq. 25) was not attempted, we expect that it would show a similarly good fit to the data as the KPZ simulation.

The time dependence of the kinetic roughening observed with light scattering during growth on an initially smooth surface at low spatial frequency ( $5.4 \mu\text{m}^{-1}$ ) also shows agreement with the second order linear term. In Fig. 7, the growth time required to saturate the kinetic roughening in the light scattering measurements matches the second order linear smoothing parameter used in the fit to the power spectral density data.

Observations of the scaling of the interface width as a function of time and spatial frequency are widely used in the literature to identify the relevant underlying growth equation (see for example [80]). Scaling measurements are typically limited by experimental constraints to two orders of magnitude or less in time and distance, with uncertain systematic errors entering at the short and long ends of the scaling interval [23,80]. In the case of GaAs growth, the surface power spectral density has a  $q^{-2}$  dependence on spatial frequency once the initial surface condition has decayed away and the surface roughness has reached steady state. This behavior is observed for  $0.2 < q < 20 \mu\text{m}^{-1}$  in the case of light scattering as shown in Fig. 6 and for  $2 < q < 100 \mu\text{m}^{-1}$  in the case of AFM measurements, and is consistent with an Edwards Wilkinson term and

non-conservative noise [36]. In the case of the mixed order growth equation (Eq. 6) we would expect an increase in slope at higher spatial frequencies as the higher order nonlinear and linear terms take over. If the high spatial frequency form follows the MBE equation with non-conservative noise, as we expect, the exponent in the  $q$ -dependence should increase from 2 to 3.33 [36]. There is no experimental evidence for such an increase in slope in the data (see for example Figs. 5 and 6b), possibly because the measurements do not extend to high enough spatial frequency.

An obvious consistency between the model and the experiment is that the experimental smoothing rate is strongly dependent on the growth rate. The smoothing rate increases by more than a factor of 10 when the Ga atom flux is initiated as shown in the light scattering measurements in Fig. 3. This can be anticipated from the model where the coefficients in the growth equation are proportional to the growth rate. This experimental result is not consistent, for example, with surface smoothing driven by gradients in the equilibrium chemical potential associated with the surface curvature, as in the Mullins equation. Another way of looking at this result is that there must be a large non-equilibrium component to the surface free energy in the presence of an atom flux.

The values of the coefficients in the growth equation are another point of agreement between the mixed order growth equation and the experiments. The coefficient of the nonlinear term  $\lambda_2 = F/\beta a^2 S_0^4$  in the growth equation (Eq. 25) depends on the growth rate, the step density and the dimensionless parameter  $\beta$ . A typical experimental growth rate is  $F = 0.2$  nm/s and the step density can be estimated independently from ex-situ AFM measurements. An AFM image of a GaAs buffer layer grown at 550°C is shown in Fig. 20. This sample is grown under typical conditions except that the As<sub>2</sub>:Ga ratio is on the high side at 6.5. We cannot be sure that the step density is the same after cool-down as it was during growth. However, the fact that no changes in surface roughness are observed in elastic light scattering during the cool-down is consistent with the view that the post-growth step density is representative of the step density during growth. By counting the steps along two orthogonal lines through the image in Fig. 20 we estimate that the average step spacing is  $70 \pm 20$  nm. Estimating the step density as if the steps formed a square crosshatch pattern, we find  $S_0 = 0.029$  nm<sup>-1</sup>. The low slope part of the surface of the growth mound in Fig. 2 shows a similar step density. This step density is typical of the step densities observed on a number of samples, although no systematic study as a function of

substrate temperature, growth rate and arsenic flux is available. This is further consistent with the 30 nm diffusion length of Ga atoms at 550°C determined from oscillations in the intensity of electron diffraction[73]. Using these parameters and taking  $\beta=5$  from the kMC simulations [59] and  $a=0.4$  nm, we find  $\lambda_2=4 \times 10^5$  nm<sup>3</sup>/s. In a fit to the experimental power spectral density,  $\lambda_2$  was found to be  $10^6$  nm<sup>3</sup>/s [40]. Taking into account the uncertainty in the measurements of the step density, the calculated value from the model is consistent with experiment [40].

In order to estimate the coefficient of the linear term  $\nu$  in the growth equation, we need a value for the dimensionless diffusion bias parameter  $\zeta$ . We have no independent information about this parameter other than its sign. In the absence of theoretical or experimental information, we assume that the physical phenomenon, which causes the stable growth, is a negative ES barrier, namely a lowering of the potential barrier for adatom hopping from an upper terrace to a lower terrace at a step edge. For simplicity we assume that there is no incorporation barrier. According to the analysis in the Appendix, in the absence of an incorporation barrier, ES barrier lowering alone gives  $0 < \zeta < 0.5$ . It would be reasonable for the barrier lowering to be a small fraction of the barrier for hopping from one terrace site to another, and also for it to be small compared to the lateral binding energy for an adatom attached to a step edge. For example, if the barrier lowering were  $E_{es} = -0.05$  eV then at  $T=550^\circ\text{C}$  using Eq. 21 and the result in the Appendix, the  $\zeta$  parameter would be  $\zeta = (1 - \exp(E_{es}/kT))/2 = 0.3$ . Of course, this value for the barrier lowering is merely an example. On the other hand, any value for the potential lowering at the step edge that is larger than  $kT$  will give a temperature independent value of  $\zeta$  saturated at its maximum value. For  $\zeta=0.3$  and a step density  $S_0 = 0.029$  nm<sup>-1</sup>, we find  $\nu = 2$  nm<sup>2</sup>/s for a 0.2 nm/s growth rate. With the experimental values for  $\nu$  in GaAs at 550°C equal to 1 nm<sup>2</sup>/s parallel to [110] and 10 nm<sup>2</sup>/s parallel to the  $[1\bar{1}0]$  direction [22], the model clearly provides a reasonable estimate. When the ES barrier is larger than  $kT$ , the ES parameter is saturated at its maximum value, and the linear smoothing coefficient provides a measure of the spacing of atomic steps on the surface during growth.

It is of interest to consider the range of validity of the continuum growth equation for the experimentally measured step density. According to the discussion following Eq. 23 the continuum growth equation is valid in the limit of long wavelengths and low surface slopes.

More specifically, the continuum growth equation description will be valid in the limit that  $\lambda > 2\pi/(\sqrt{\beta}S_0) \sim 100$  nm and  $\nabla h < aS_0 \sim 1^\circ$ . These limits apply to GaAs growth under typical conditions of 1  $\mu\text{m/hr}$  and 550°C substrate temperature.

For the values of  $\nu$ ,  $\lambda_2$  in the GaAs growth experiments on thermally de-oxidized surfaces discussed here, with peak surface amplitudes of  $\sim 50$  nm and wavelengths of  $\sim 1000$  nm, the smoothing rate is dominated by the linear  $\nu$  term. In the example discussed above with  $\zeta=0.3$ , a net hopping rate at a downhill step that is 50% bigger than the hopping rate at an uphill step is sufficient to give the experimentally observed smoothing rate. By extension, a displacement of an incoming vapor atom by one lattice constant in the up-slope direction in the vicinity of an atomic step (“steering effect”) would easily be sufficient to destabilize the growth [52,53].

The surface shape evolution can also be described by the coupled growth equations directly (Eqs. 22, 24) without combining them into a single dynamical equation for  $h$ . This approach relaxes the low slope approximation that is used in the derivation of the growth equation from the adatom transport equation and extends the range of validity of the continuum model to higher slope surfaces. Of course, the continuum model presented above is inherently limited to low slopes by the presence of new low index crystal planes at higher slope where the concept of flat terraces separated by atomic steps breaks down and is replaced by a new low index crystal plane with different atomic steps. With increasing surface slope, the next low index crystal planes in GaAs, the  $\{110\}$  planes, are at an angle of  $45^\circ$  with respect to the  $(100)$  plane. Therefore physical constraints also restrict the range of validity of the model to  $\nabla h \ll 1$ . It is unclear which constraint, physical or mathematical, is more restrictive.

The coupled continuum growth equations (Eqs. 22, 24) do a good job of fitting the shape of re-grown layers on patterned GaAs as shown in Figs. 15 and 16 [58]. The adatom transport equation used in the simulations in Figs. 16 and 17 contains expressions for the step edge capture and release rates that are first order in the step density rather than quadratic as discussed above. Although the parameter values are different in the two treatments, the surface shapes produced with the two different expressions for the adatom capture and release rates are similar. In the temperature dependence shown in Fig. 17, note that the low temperature growths tend to reproduce the shape of the starting surface, whereas in the high temperature growths the initial surface shape is rapidly distorted during growth [55]. This makes intuitive sense because at low

temperatures the adatoms tend to attach close to the point where they land on the surface whereas at high temperatures the adatoms tend to diffuse a relatively large distance from their point of initial arrival, thereby distorting the initial shape.

There are three other features in the data which are also reproduced by the model. At long growth times, both the model and the experiment show V-shaped valleys and rounded ridges. At intermediate growth times, the model reproduces the “inverted gothic window” shape of the valleys in the experimental scan lines and at low growth temperatures a small mound develops in the valleys [61,81]. The mound is caused by the fact that the sloping parts of the surface have high step density and tend to collect adatoms that diffuse in from nearby flat regions with low step density. Therefore, the adatom density is depleted close to a steeply sloping region, leaving a valley. This phenomenon explains the overshoot in peak-to-peak surface amplitude reported by Kan and collaborators during the initial stages of regrowth on a series of patterned substrates with different feature sizes [39,81]. Numerical solutions of the continuum growth model (Eqs. 12, 22, 24) are shown in Fig. 21 and have the same overshoot in the peak-to-peak amplitude of the surface during growth as observed in the experiments, even though the model is globally stable and the ES barrier is assumed to be negative (stable) [82]. Overshoots are not observed in numerical solutions of the KPZ equation; therefore the overshoot is believed to be an indication of the presence of the fourth order (conservative) nonlinear term. An overshoot is also possible with the fourth order linear term (Mullins equation), but not with the second order linear term alone. The peak-to-peak surface amplitude is plotted as a function of time in Fig. 21 using the same growth parameters used to produce the simulations in Figs. 16 and 17. Data points from Kan’s paper are included in the figure for comparison [39].

A difference between the continuum model and the experimental data has been noted above in connection with the kMC simulations in Figs. 16, namely there are sharp peaks at the top of the ridges and distinct shoulders on the side of the ridges in the data [61,81]. These features are also present in the kMC simulations, but are not present in the continuum model. As discussed above they are believed to be associated with the step density minimum, which occurs at non-zero slope in the kMC simulations. This effect has not been included in the continuum model.

Finally, we comment on the smoothing effect observed for growth in the presence of an In, Sb, Te or Bi surfactant in the context of the growth model [50, 83-85]. Bismuth is a

particularly good surfactant for GaAs growth in that it has a strong smoothing effect with no incorporation of Bi under standard GaAs growth conditions [84]. The surfactants most likely reduce the hopping energy of adatoms on the surface as well as the binding energy of adatoms to step edges, and thereby mimic the effect of a higher growth temperature. This will increase the diffusion length of adatoms and reduce the step density  $S_0$ , which in turn will increase the coefficient of the linear smoothing term  $\nu$  in the growth equation (Eq. 25). Surfactants might also increase the smoothing rate by altering the potential barriers at step edges, which could increase the coefficient  $\zeta$  in the growth equation [50].

## 6. Conclusions and Open Questions

A continuum growth equation has been derived from the adatom transport equation with adatom incorporation into the surface at step edges. The growth equation has been developed to describe experimental data on surface morphology during epitaxial growth of GaAs(100). The transport equation includes the adatom transport processes in the classic Burton Cabrera and Frank [1] picture of crystal growth plus a combination of a negative Ehrlich-Schoebel barrier for interlayer transport, or an ES barrier in combination with an incorporation barrier for adatoms at step edges, that together favour downhill adatom migration at step edges. The asymptotic growth equation contains a stable second-order linear term (Edwards-Wilkinson term) and a fourth-order conservative nonlinear term. This analysis fills a gap in previous treatments of surface shapes in terms of continuum growth equations in that the explicit expressions for the coefficients in the growth equation are obtained from a systematic analysis of the microscopic adatom dynamics. These parameters, in turn, depend on the density of steps, the growth rate and the asymmetric potential barriers to adatom migration in the vicinity of step edges (ES barrier and incorporation barrier). Although the growth rate and step density can be measured independently and the step edge release rate has been inferred from electron diffraction experiments and from density functional calculations, the potential barriers at step edges can only be inferred indirectly from the surface smoothing experiments. The model is found to be in excellent agreement with a large body of experimental data on the shape of GaAs surfaces during epitaxial growth. The areas of agreement include the power spectral density of the surfaces as a function of growth time, the strong dependence of the smoothing rate on the growth rate, the shape of microfabricated gratings as a function of time and temperature during growth, the overshoot in the smoothing of patterned surfaces and the consistency between the values of the

coefficients in the growth equation and the independently determined atomistic parameters. Although this treatment has been developed for GaAs epitaxy, the derivation is quite general and should be relevant to other materials which show stable epitaxial growth.

Although the model presented in this review explains a large body of experimental data on GaAs in terms of atomic scale processes, many experimental and theoretical issues remain unresolved. In the analysis of the surface shape evolution, the step density is a critical parameter. Better experimental data on step density as a function of temperature, growth rate and surface slope is needed (e.g., Fig. 13). A related measurement is the temperature and growth rate dependence of the coefficients of the linear and nonlinear terms in the growth equation. Since the coefficient of the nonlinear term in the growth equation depends on the fourth power of the step density, this parameter is particularly sensitive to the step density. The best way to measure the parameters in the growth equation may be through studies of the smoothing of patterned surfaces. The power spectral density of the surface of GaAs has the  $q^{-2}$  dependence expected with the second order linear term in the growth equation; however, the physical origin of the noise processes which set the amplitude of the power spectral density is not understood at all. A better understanding of the role of fluctuations in the continuum growth equations is needed. For example, it has been suggested that the random nucleation of islands introduces a short length scale smoothing term, although a systematic derivation of this effect is lacking [55]. The power spectral density is more than an order of magnitude larger than one would expect with kinetic roughening associated with the shot noise from the adatom deposition. The role of the various random processes involved in crystal growth - shot noise from the deposition flux, random nucleation of islands and random step edge attachment/detachment - in the kinetic roughening of systems that show stable growth is not understood. Finally, it would be interesting to see if a similar growth equation can be used to describe the surface morphology of other materials.

Although we have assumed that the second order linear term in the growth equation that causes GaAs growth to be stable comes from a negative ES barrier at step edges, other mechanisms are possible. New experimental methods that can distinguish between the various physical mechanisms that cause stable and unstable growth are needed.

#### **Appendix: Ehrlich-Schwoebel Parameter in terms of Step Edge Capture Velocities**

In this appendix we obtain an expression for the ES parameter  $\zeta$  in Eq. 21 in terms of the barrier height for adatom hopping across a step edge (ES barrier). On a site  $i$  on a flat terrace far from a step edge, the rate of change of adatom density in 1D perpendicular to the step edge is

$$\partial_t N_i = \frac{\omega_0}{4} N_{i-1} - \frac{\omega_0}{2} N_i + \frac{\omega_0}{4} N_{i+1}, \quad [\text{A1}]$$

where  $\omega_0$  is the hop rate of an adatom with no lateral neighbors. For a 2D SOS model, the hop rate to the left is  $1/4$  of the total hop rate, for example. From the definition of the second derivative, this last expression is equivalent to the 1D diffusion equation,  $\partial_t N = D \partial_x^2 N$  with  $D = \omega_0 a^2 / 4$  in the continuum limit. For an adatom one site away from the boundary, the rate equation becomes

$$\partial_t N_1 = -\frac{\omega_0}{2} N_1 + \frac{\omega_0}{4} N_2. \quad [\text{A2}]$$

There is a flux into the boundary, assumed to be absorbing, of  $-\omega_0 N_1 / 4$ . In this case, the surface absorption velocity, in Eq. 14, is  $v_0 = \omega_0 a / 4$ . If instead we calculate the surface absorption velocity from site 2, two jumps are required to reach the step edge. An atom that makes a jump towards the step has a 50% probability of making another jump in the same direction. The rate at which adatoms at site  $N_2$  reach the step is  $-\omega_0 / 8$ . However, these adatoms must move two steps so the surface absorption velocity is the same, as it should be.

If there is an incorporation barrier at the step edge,  $E_{inc}$ , as shown in Fig. 11, then an adatom in a site one removed from the step edge will experience an additional barrier to hopping to the step edge where it can bind laterally to the step edge. In this case an adatom at a site 2 removed from the step edge will still hop with a rate  $\omega_0 / 4$  in the direction of the step edge. Once it is on the site one removed from the step edge, the probability of hopping to the step edge will be  $f / (1 + f)$  where  $f = \exp(-\Delta E_{inc} / kT)$ . If the incorporation barrier is positive,  $\Delta E_{inc} > 0$ , then  $f < 1$ . We don't need to worry about the lateral hopping rate since hops parallel to the step edge (assumed to be straight) will not change the probability of step capture and only the relative forward/backward hop rates matter. Therefore in the presence of the incorporation barrier the capture velocity is  $v_0 = \omega_0 f a / (2(1 + f))$ .

The problem is similar when an adatom approaches a step edge from the terrace above. In the case of an adatom in a site two removed from the lateral attachment location at the bottom of the step, it will move to the right (towards the step) with rate  $\omega_0/4$ . If it jumps towards the step then it forms a double height step, which is not allowed except on a transient basis. To prevent double height steps from forming, the adatom must move again. This time the ES barrier changes the downhill rate by the factor  $e = \exp(-\Delta E_{es}/kT)$ . In the case that the ES barrier is negative, favoring downhill migration,  $\Delta E_{es} < 0$  and  $e > 1$ . The probability that the adatom at 2 that jumps towards the step edge will go over the step and attach at the laterally bonded location at the bottom will be  $e/(1+e)$ . Motions parallel to the step do not change the rate of going over, they merely shift the location if the step is straight. Therefore the rate that the adatom at a location 2 sites away from the step edge is absorbed by the step is  $\omega_0 e / (4(1+e))$ . By analogy with the attachment to the step edge from the terrace below, discussed above, the surface absorption velocity in this case will be  $v_L = \omega_0 e a / (2(1+e))$  since the adatom moves 2 lattice sites in the step edge capture process. If  $e=1$  we get the same result as in the case with no step edge barrier. This means that the restriction applied to the SOS model to prevent double height steps, except on a transient basis, does not contribute to a net lateral flux of adatoms, as we have been assuming.

We have already obtained an expression for the diffusion constant from the rate equation for the adatoms. It is of interest to derive this result in a different way. For 1D diffusion,  $\langle x^2 \rangle = Na^2 = 2Dt$  (see for example Ref. [86]), where  $a$  is the lattice constant,  $t$  is the diffusion time and  $N$  is the number of jumps. In our case,  $N = \omega_0 t / 2$ , where the total lateral (left-right) jump rate is  $\omega_0 / 2$ . Solving for  $D$ , we obtain the same result as before,  $D = \omega_0 a^2 / 4$ . In 2D, the result is  $\langle x^2 + y^2 \rangle = Na^2 = 4Dt$ . In this case, the total jump rate is  $\omega_0$  and the diffusion constant is the same:  $D = \omega_0 a^2 / 4$ .

From Eqs. 19, 20, the dimensionless diffusion bias parameter  $\zeta$  is

$$\zeta = \frac{DL(v_L - v_0)}{a(v_0 D + v_0 v_L L + v_L D)}. \quad [\text{A3}]$$

This expression can be written more simply in terms of the Ehrlich-Schwoebel and incorporation lengths,  $\ell_{es} = D/v_L$  and  $\ell_{inc} = D/v_0$  respectively:

$$\zeta = \frac{L(\ell_{inc} - \ell_{es})}{a(\ell_{inc} + \ell_{es} + L)}. \quad [\text{A4}]$$

In the limit that the ES barrier and incorporation barriers are large and positive the two lengths  $\ell_{es}, \ell_{inc}$  also become large. As long as  $\ell_{inc} > \ell_{es}$  the net adatom diffusion current is downhill. If the ES barrier and incorporation barrier are not more than a few times  $kT$  and the surface slope is not too large then  $\ell_{es}, \ell_{inc} < L$  and the expression for  $\zeta$  can be further simplified, as follows:

$$\zeta = \frac{1}{2} \left( \frac{1}{f} - \frac{1}{e} \right). \quad [\text{A5}]$$

Once again, as long as the incorporation barrier is larger than the ES barrier ( $f < e$ ), adatoms will tend to diffuse downhill and the growth will be stable.

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## Figure Captions

Figure 1. Comparison of MBE growth on thermally desorbed starting surfaces and simulations using an anisotropic KPZ model with non-conservative noise. Atomic force microscope images of MBE-grown surfaces at  $T=550^{\circ}\text{C}$ ,  $F=1\text{ ML/s}$  ( $1\ \mu\text{m/hr}$ ) with an  $\text{As}_2:\text{Ga}$  ratio of 2.9:1 (a) Starting surface ( $t=0\text{ min}$ ,  $\text{RMS}=5\text{ nm}$ ), (b) 10 min growth ( $\text{RMS}=1.5\text{ nm}$ ), (c) 37.5 min growth ( $\text{RMS}=1.1\text{ nm}$ ) and (d) 150 min ( $\text{RMS}=0.6\text{ nm}$ ). KPZ simulated surfaces with  $F=1\text{ ML/s}$  ( $1\ \mu\text{m/hr}$ ),  $\nu=4\text{ nm}^2/\text{s}$  and  $\lambda=12\text{ nm/s}$ : (e) 10 min growth ( $\text{RMS}=1.5\text{ nm}$ ), (f) 37.5 min growth ( $\text{RMS}=1.1\text{ nm}$ ) and (g) 150 min growth ( $\text{RMS}=0.6\text{ nm}$ ). All images are  $10 \times 10\ \mu\text{m}$ . The surface features are elongated along the  $[1\ \bar{1}0]$  direction. [In this paper, a monolayer (ML) of GaAs is assumed to be a single Ga-As bilayer, corresponding to one-half of a conventional cube unit cell in the  $[100]$  direction.]

Figure 2. AFM image of a thermally cleaned GaAs (100) substrate, after growth of a buffer layer, showing an  $\sim 3\text{ nm}$  tall mound with characteristic rounded top and V-shaped valleys. Atomic steps are clearly visible in this image. The surface was grown for 75 minutes at  $T=550^{\circ}\text{C}$  and  $F=1\text{ ML/s}$  ( $1\ \mu\text{m/hr}$ ) with an  $\text{As}_2:\text{Ga}$  ratio 2.9:1. The scale markers are in microns.

Figure 3. Diffusely scattered light intensity during MBE growth of GaAs. The scattered light intensity is sensitive to surface roughness at a spatial frequency of  $41\ \mu\text{m}^{-1}$  which is defined by the wavelength and the angles of incidence and scattering. The abrupt increase in surface roughness at 25 min corresponds to the oxide desorption which takes place while the sample temperature is being ramped up. This is followed by a relatively fast smoothing during a high temperature ( $620^{\circ}\text{C}$ ) anneal for 30 min, followed by slower smoothing during annealing at the growth temperature ( $550^{\circ}\text{C}$ ). The abrupt increase/decrease in smoothing rate as the Ga shutter is opened/closed is clearly visible. An expanded view of the change in smoothing rate as the Ga shutter is opened and closed is shown in the lower panel. The growth rate with the Ga shutter open was about  $1\text{ ML/s}$  ( $1\ \mu\text{m/hr}$ ).

Figure 4 Light scattering during growth of a GaAs buffer layer on a thermally deoxidized substrate showing the effect of growth on a contaminated surface. The growth rate was about 1 ML/s (1  $\mu\text{m/hr}$ ) at a substrate temperature of 600°C. The substrate cleaning procedure was most effective for sample *a* and least effective for *c* [4].

Figure 5 Power spectral densities from AFM images of three different samples consisting of a thermally cleaned GaAs substrate, and two buffer layers grown for 10 min and 150 min at 550°C and 1 ML/s (1  $\mu\text{m/hr}$ ) on thermally cleaned substrates (symbols) together with fits to the data using the KPZ equation (lines). The As<sub>2</sub>:Ga ratio during growth was 8:1, as measured with an ion gauge with no correction for the relative ionization efficiencies. The upper figure (a) shows the power spectral density along the  $[1\bar{1}0]$  direction and (b) shows the power spectral density along the  $[110]$  direction [23].

Figure 6 Power spectral density obtained from diffuse light scattering measurements in the plane of incidence for three different samples prepared as indicated. The 30 min growth was carried out with a substrate temperature of 590°C and a growth rate of 1 ML/s (1  $\mu\text{m/hr}$ ). The power spectral density of the thermally de-oxidized surface agrees remarkably well with the power spectral density in Fig. 5 for a similarly prepared surface determined by atomic force microscopy [29,34].

Figure 7 Power spectral density measured with diffuse light scattering on a 2  $\mu\text{m}$  thick GaAs buffer layer on a thermally de-oxidized substrate, for in-plane momentum transfer parallel to the  $[1\bar{1}0]$  and  $[110]$  directions. The buffer layer was grown at 590°C at a rate of 1 ML/s (1  $\mu\text{m/hr}$ ). The solid line has slope  $-2$ . The characteristic spatial frequency of the surface mounds, illustrated in Figs. 5, 6, is almost completely gone after a thick layer has been deposited [29,34].

Figure 8 Scattered light intensity for in-plane momentum transfer of 5.4  $\mu\text{m}^{-1}$  as a function of time during growth of a GaAs buffer layer at 1 ML/s (1  $\mu\text{m/hr}$ ) and 600°C substrate temperature. The substrate was cleaned with atomic hydrogen so as to avoid the surface pitting observed with thermal oxide desorption. The solid lines are fits to the data using Eq. 3 with  $\nu$  equal to 6.2

$\text{nm}^2/\text{s}$  and  $5.7 \text{ nm}^2/\text{s}$  for in-plane momentum transfer along the  $[1\bar{1}0]$  and  $[110]$  directions, respectively. The slow random variation in scattered intensity may be due to speckle. This figure is taken from C. Lavoie's PhD thesis [34], and is published here for the first time.

Figure 9. Power spectral density along the  $[110]$  direction for epitaxial GaAs films grown on thermally de-oxidized substrates. The experimental data in (a) is the same as in Fig. 5(a). KPZ simulations are indicated by the dotted and solid lines, for 10 and 150 min of growth, respectively at 1 ML/s ( $1 \mu\text{m}/\text{hr}$ ). (b) The experimental data for the starting surface (top) is the same as in (a). The lower set of data points in (b) is the power spectral density after 90 minutes of growth at 0.8 ML/s ( $0.8 \mu\text{m}/\text{hr}$ ) on a thermally de-oxidized substrate. The solid line is a simulation using the mixed order growth equation (Eq. 6). The substrate temperature was  $550^\circ\text{C}$  for all growths. The power spectral densities for spatial frequencies  $q < \sim 2 \mu\text{m}^{-1}$  may not be reliable [40].

Figure 10 Schematic diagram showing the basic atomic scale processes involved in epitaxial crystal growth as considered in this review. The rate of step edge crossing (or equivalently, interlayer transfer) will be affected by an Ehrlich-Schwoebel potential that may exist at the step edge.

Figure 11 Schematic diagram showing the potential energy for adatoms in the vicinity of an atomic step. The relevant energy barriers are indicated.  $E_{sub}$  is the potential barrier for adatom hopping on a flat terrace,  $E_{inc}$  is the potential barrier for adatom hopping into a step edge site from the lower terrace and  $E_{es}$  is the increase in the potential barrier for hopping from the upper terrace to the lower terrace, also known as the Ehrlich-Schwöbel barrier. In this diagram, the ES barrier is positive and the incorporation barrier is negative. In principle the barriers can have either sign depending on the details of the interatomic potentials in the vicinity of the step edge. The experimental data suggests that  $E_{es} < E_{inc}$  in the case of GaAs.

Figure 12. Effect of spatial frequency and amplitude of surface topography on surface evolution. Projected 2D solid-on-solid kMC simulations with three different sinusoidal initial topographies: (a) 600 atom period, 4 atom amplitude (i.e., 9 discrete atomic levels); (b) 300 atom period, 4

atom amplitude; and (c) 300 atom period, 8 atom amplitude. Part (d) shows the smoothing rate as a function of the pitch (or spatial frequency) for low amplitude gratings similar to (a). An atom diameter is assumed to be 0.3 nm.

Figure 13. Steady-state step density from solid-on-solid kMC simulations of vicinal surfaces at four different temperatures. The line through the origin is the step density for a straight-stepped vicinal surface (staircase). (b)-(d) show sections of three surfaces from simulations at 500°C taken (b) before, (c) at, and (d) after the step-density minimum, at slopes indicated in (a) by circles.

Figure 14 Left hand panel (a) shows a fit of the mixed order growth equation (colors) to a kMC simulation of the smoothing of a sinusoidal grating at a growth temperature of 495°C and 1 ML/s (black) using  $\nu=1 \text{ nm}^2/\text{s}$  and  $\lambda_2=280 \text{ nm}^3/\text{s}$ . Panels (b)-(d) show how the first three Fourier coefficients in a Fourier series expansion of the kMC surface (black) and the continuum growth equation simulation (colors) compare as a function of growth time for three different growth temperatures. The coefficients in the growth equation were determined by matching the time dependence of the Fourier coefficients for the kMC simulation with the simulation using the continuum growth equation [59].

Figure 15. Temperature dependence of  $\nu$  and  $\lambda_2$  at various growth rates obtained by fitting the solid-on-solid kMC simulations (solid squares 0.01; circles 0.1; crosses 1; and solid diamonds  $F=10\text{ML/s}$ ) and the theoretical predictions based on the continuum model (thick solid line 0.01; dash-dotted 0.1; dashed 1; and thin solid line  $F=10\text{ML/s}$ ). In the continuum model for  $\lambda_2$ , we use  $\beta=6$  [59].

Figure 16. (a) AFM cross sections of microfabricated gratings after deposition of progressively thicker layers at a substrate temperature of 580°C, a growth rate of 1 ML/s (1  $\mu\text{m/hr}$ ) and an  $\text{As}_2\text{:Ga}$  pressure ratio of 3:1. The initial condition consisted of 100 nm deep gratings oriented perpendicular to the [110] direction; (b) scan lines from computed from fits based on the coupled growth equations; (c) scan lines from 2D kMC simulation of a smaller 10 nm high

grating structure, where one  $\Delta t$  equals 5.6 ML of growth. Offsets between scan lines are arbitrary [61].

Figure 17. Similar to Figure 15, except a fixed film thickness at different growth temperatures. (a) AFM cross sections for regrowth on 100 nm deep gratings oriented perpendicular to the  $[1\bar{1}0]$  direction; (b) simulation based on coupled growth equations with similar parameters as in Figure 15. The grating pitch is 5  $\mu\text{m}$ . All growths are 1 hr at 0.8ML/s (0.8  $\mu\text{m/hr}$ ) at an  $\text{As}_2\text{:Ga}$  pressure ratio of 3:1. Offsets between scan lines are arbitrary [61].

Figure 18 The same power spectral density data as in Figure 5 (symbols) with fits using the MBE equation (lines) with conservative noise. The fitted curves show a stronger  $q$  dependence than the experimental data. The KPZ fits in Figure 5 are a better match to the data [23].

Figure 19 (a) AFM scan lines for the starting surface and GaAs buffer layers grown on thermally de-oxidized GaAs for 3, 10, 37.5 and 150 min for five different samples grown at 550°C and 1 ML/s (1 $\mu\text{m/hr}$ ). (b) Simulated scan lines calculated from the KPZ equation using the experimental AFM data for the starting substrate from (a) as the initial condition, and the same parameters as in the simulations in Figs. 1, 5. (c) Simulation using the MBE equation with the experimental scan line as the initial condition. (d) Simulation with Edwards-Wilkinson equation. Scans are offset for clarity, and the vertical scale is exaggerated [23].

Figure 20 AFM images of a GaAs buffer layer grown at 550°C on a H-cleaned substrate showing individual atomic steps. The growth rate was 1 ML/s (1 $\mu\text{m/hr}$ ). The inset shows the power spectral density from 0 to 300  $\mu\text{m}^{-1}$ . The arrow shows the fast diffusing  $[1\bar{1}0]$  direction. The step geometry is relatively isotropic in the plane because a high  $\text{As}_2\text{:Ga}$  overpressure was used in the growth (6.5:1). By counting steps in the two orthogonal directions we estimate that the average step spacing is 70 nm [23].

Figure 21. (a) Simulated peak-to-peak height of gratings as a function of grating pitch for different thickness of deposited material as indicated in the legend. The simulation uses the

same coupled growth equations and the same parameters as the simulation in Fig. 15. (b) Experimental data on peak-to-peak surface height from Ref. 38 as a function of pit diameter. The inset shows the evolution of the surface shape in the simulation. Both the simulation and the experimental data show that the smoothing of the “pits” is not monotonic: there is an overshoot in the initial stages of the smoothing during which the peak-to-peak amplitude first increases before it decreases [79].