LETTER TO THE EDITOR

Nonlinear diffusion equation for crystal growth on stepped surfaces

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Abstract. An equation that includes both adatom diffusion and diatomic island formation is derived for describing growth on stepped surfaces. The equation is integrated numerically to obtain adatom and island concentration profiles along the terraces. Comparison of this solution with experimental measurements on vicinal GaAs(001) for a variety of Ga and As$_2$ fluxes and with Monte Carlo simulations shows that inclusion of island formation in the growth equation is crucial in determining the temperature beyond which growth becomes dominated by step propagation.

The pioneering theory of Burton, Cabrera and Frank (BCF) [1] for near-equilibrium crystal growth on stepped surfaces used linear diffusion equations to determine the step velocity and the distribution of adatoms on terraces. The advent of molecular-beam epitaxy (MBE), in which growth occurs under manifestly far-from-equilibrium conditions, has led to renewed interest in the BCF theory since, for appropriately chosen values of beam fluxes, substrate temperature, and terrace length, growth occurs by the advancement of steps across terraces [2-4]. Extensions of the BCF theory to MBE have included the influence of the moving step boundary [5-7] (important in semiconductor growth, where step velocities are high), deviations from equilibrium at the step edges [8], and consideration of two-dimensional homogeneous nucleation theory [9, 10]. In none of these treatments, however, was lateral interactions of adatoms on the terraces included in the calculations, though it was recognized that corrections to BCF theory due to island-formation would be substantial for growth under typical conditions found for MBE [6, 9-11].

In this letter, we generalize the BCF theory by including a first-order approximation to lateral adatom interactions in the form of diatomic island formation. By using simulations of MBE [12] to quantify the effect of island-formation, the theory reproduces measured values of the transition temperature, T_c, at which growth becomes dominated by step advancement for GaAs using different Ga and As$_2$ fluxes. This remarkable result shows that the inclusion of island-formation is essential for obtaining a realistic model of epitaxial growth on misoriented surfaces.

The vicinal surface consists of an infinite train of flat steps separated by terrace length h in the x-direction (figure 1). The substrate is treated as a continuum on which there is a concentration $n(x, t)$ of surface adatoms. The continuity equation for $n(x, t)$ on a section of the vicinal surface is

$$\frac{\partial n(x, t)}{\partial t} = D\frac{\partial^2 n(x, t)}{\partial x^2} + J - R[n(x, t)] \tag{1}$$
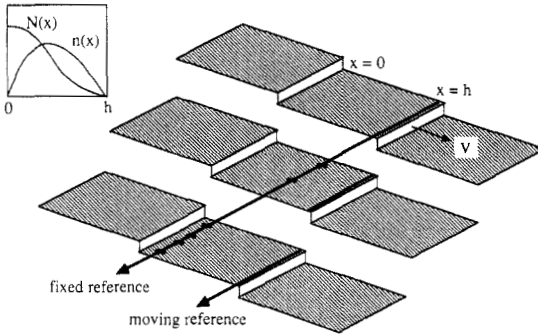
Figure 1. Schematic representation of a section through the stepped crystal and the concentration of adatoms, $n(x)$, and of diatomic islands, $N(x)$, along a terrace.

where D is the diffusion constant of adatoms on the terraces, J is the adatom flux to the surface, and $R(n)$ is a concentration-dependent 'reaction rate' for island formation, which will be specified below. Desorption from the surface has been omitted due to the long adatom residence times found for typical MBE growth conditions. The diffusion constant is taken to be of the Arrhenius form $D = \nu a^2 \exp(-E_D/k_B T)$, where ν is an adatom vibrational frequency, a is the nearest-neighbour hopping distance, E_D is the activation energy for surface diffusion for a lone adatom, k_B is Boltzmann's constant, and T is the substrate temperature. For a steady state in which the steps move at a constant velocity v, we transform to a frame of reference which moves with the step train, in which case the continuity equation (1) becomes

$$D\frac{d^2 n}{dx^2} + v\frac{dn}{dx} + J - R(n) = 0. \tag{2}$$

In the BCF theory, the concentration of adatoms at the step edge is determined by the local equilibrium condition. However, the assumption of thermal equilibrium is not likely to be valid under the growth conditions of MBE. Therefore, we impose absorbing boundary conditions at the step edges: $n(x = 0) = n(x = h) = 0$.

We include island formation on the terraces to a first-order approximation by allowing the formation only of diatomic islands. In regimes where growth is not dominated by the formation and coalescence of clusters, this is not too restrictive an assumption. For example, the inclusion of triatomic islands changes T_c by only a few per cent. Denoting the island concentration by $N(x, t)$, the rate of formation of diatomic islands on the terrace is thus given by

$$R(n) = 2\frac{dN}{dt} = 2\sigma D n^2 + 2Jm\frac{n}{n_0}. \tag{3}$$

The first term on the right-hand side of (3) represents the rate at which single mobile adatoms collide to form islands and is proportional to D and to σ, a capture efficiency of order one [13]. The second term accounts for the direct collision of incoming atoms with adsorbed adatoms and is proportional to the total fraction of incoming adatoms that arrive at island-forming sites, n/n_0, where n_0 is the concentration of lattice sites. The factor m is the number of sites around a single adsorbed adatom that form a diatomic island when filled. For example, for a (001) surface, $m = 4$, since a single adatom has four nearest neighbours; if the site of the adatom itself is included, then $m = 5$.

In order to solve (2), we require an additional relation to give the unknown velocity v. Mass conservation at the step edge yields the following expression for the velocity

$$vn_0 = D\frac{dn}{dx}\bigg|_{x=0} - D\frac{dn}{dx}\bigg|_{x=h} + 2\sigma D\int_0^h n^2(x)\,dx + 2mJ\int_0^h (n/n_0)\,dx. \tag{4}$$

The first and second terms on the right-hand side of (4) are the fluxes of single adatoms into the step from below and above, and the last two terms are the fluxes due to islands. We recognize the right-hand side of (4) as the integral of (2), apart from the flux term, along a terrace from $x = 0$ to $x = h$, with $R(n)$ given by (3), from which we deduce that $vn_0 = Jh$.

Combining (2) and (3) with the determined value of v and introducing the dimensionless concentration $y \equiv Dn/(Jh^2)$ and distance $x \to x/h$ yields

$$\frac{d^2y}{dx^2} + \alpha\frac{dy}{dx} + 1 - 2\alpha\beta y^2 - 2\alpha m y = 0 \qquad y(0) = y(1) = 0. \tag{5}$$

The dimensionless parameter $\alpha = Jh^2/Dn_0$ represents the ratio of the diffusion time for an adatom to reach a terrace (h^2/D) to the interarrival time of atoms per site (n_0/J), and the dimensionless parameter $\beta = \sigma n_0 h^2$ is a measure of the misorientation angle (through the terrace length with monatomic steps) and of the lateral interaction (through the capture efficiency). The variables in (5) are scaled so that the diffusion term and flux term are both order one independent of the value of α. We can thus identify three growth regimes: (i) $\alpha > 1$, island-formation dominates; (ii) $1 > \alpha > 1/\beta$, island-formation competes with step-advancement; and (iii) $\alpha < 1/\beta$, step-advancement dominates.

Numerical solution of (5) is now straightforward using, for example, a fourth-order Runge–Kutta method with Kutta's coefficients [14]. Figure 2 shows the effect of increasing α and thus the temperature (through the diffusion constant D): (a) with no island-formation [$R(n) = 0$ in (2)] and (b) with island-formation ($\sigma = 1$, $m = 5$), for a fixed terrace length $h = 15a$. The lowering and flattening of the profile is more marked at lower temperatures (higher α) due to island formation.
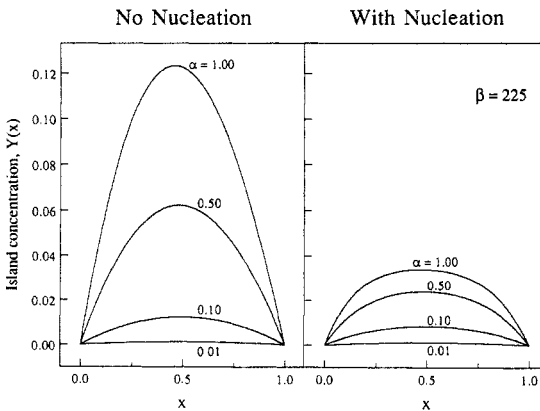

Figure 2. Adatom concentration profiles along a terrace with length $h = 15a$ for various α. The left panel shows profiles with no island-formation included ($\alpha = 0$ and $m = 0$ in (5)). Note the flattening and lowering of the profile in the right panel, which includes island formation ($\alpha = 1$ and $m = 5$ in (5)).

Once the adatom concentration is known, the island concentration profile along a terrace may be determined from (3). Islands are stable and immobile once formed; thus the islands *do not move with the step*. With reference to figure 1, we focus on the position $x = h$ in a stationary coordinate system and observe the formation of islands *with time*. Since at $x = h$ the step is freshly formed there can be no islands on top of it; thus $N(h, t = 0) = 0$. As the step moves with velocity v the concentration of islands includes all islands which were formed during the time $t = (h - x)/v$ the step moves a distance $h - x$. Thus, in the moving coordinate system we replace t by $(h - x)/v$ in (4) and obtain in terms of the dimensionless quantities defined in (5) the dimensionless island concentration $Y(x) \equiv 2N(x)/(\alpha n_0)$

$$Y(x) = 2\beta \int_x^1 y^2(x) \, dx + 2m \int_x^1 y(x) \, dx. \tag{6}$$

When $t = h/v$ ($x = 0$ in the moving reference frame), the next step has reached our fixed reference point, and all islands are instantaneously captured by the advancing step. The island concentration is greatest directly below the step edge at $x = 0$, as shown schematically in figure 1.

The growth mode in MBE is strongly temperature dependent. At low temperatures, the surface diffusivity is small so growth due to island formation competes with adatom diffusion to the step edges. With increasing temperature, the enhanced mobility of adatoms promotes direct incorporation at the step edges and island-formation diminishes, which leads to growth by step advancement. The transition to the step-flow growth mode is gradual; however, we expect that step advancement is dominant at a temperature T_c when the island-formation rate becomes negligible compared to the diffusion rate of single adatoms to the steps, which corresponds to regime (iii) above. Evaluation of the magnitude of the terms in (5) shows that $\alpha_c < 1/\beta \ll 1$ to give a negligible island-formation rate $R(y)$. The temperature T_c is then evaluated from α_c as

$$T_c = \frac{E_D}{k_B} \left[\ln \left(\frac{\nu \alpha_c}{Jh^2} \right) \right]^{-1}. \tag{7}$$

Treating surface diffusion using the Einstein relation $x^2 = 2D\tau$, with $x = h$, D given as above, and $\tau = n_0/J$, the average time interval between deposition at a specific site, yields for T_c the expression

$$T_c = \frac{E_D}{k_B} \left[\ln \left(\frac{2\nu}{Jh^2} \right) \right]^{-1}. \tag{8}$$

By neglecting island formation, (8) predicts that growth by step advancement is achieved when the time for single adatoms across a terrace is of the same order of magnitude as the adatom interarrival time at a specific site, $\alpha = (h^2/D)(n_0/J) = 2$. However, the island-formation rate $R(y)$ actually dominates the growth equation (5) for $\alpha = 2$ (figure 2). Thus, the central assumption of the Einstein relation, that the effect of adatom interactions can be neglected in calculating T_c, is inconsistent; it is necessary to utilize (5), which incorporates the full nonlinear physics.

We compare the results of our model to Monte Carlo simulations of [12, 15, 16]. T_c is identified in the simulations as the temperature beyond which oscillations of the step density disappear. We have shown above that $\alpha_c < 1/\beta \ll 1$; however, utilization of (5) requires that we pinpoint a value of α_c at which we can consider step advancement to be the dominant mode of growth. In this regime, the island-formation rate is very small and the dimensionless island concentration (6) immediately below a step edge,

$2N(x)/n_0 = \alpha Y(0)$ (which is the maximum island concentration on the terrace), takes a small value Y_0. The temperature T_c is then found by determining the value of $\alpha = Jh^2/Dn_0$ for which $\alpha Y(0) = Y_0$ as follows: (a) solve (5) for a given α and with fixed $\beta = \sigma n_0 h^2$, and (b) determine $Y(0)$ from (6). This process is repeated until α_c is found which yields $\alpha Y(0) = Y_0$. We find that $Y_0 = 0.01$ (with corresponding $\alpha_c = 1/(2\beta)$) gives excellent agreement with the simulations over an order of magnitude variation in the flux J and for misorientation angles of $2°-4°$, as shown in table 1 [16]. This is remarkable given the sharp dependence of the transition temperature on the value chosen for Y_0 (figure 3). Thus step flow is considered to dominate when the atomic flux into the step edge due to upswept islands is below approximately one percent, a physically reasonable criterion. Our nonlinear theory also shows that the diffusivity in the Einstein relation $x^2 = 2D\tau$ should be replaced by an effective diffusivity $D_{\text{eff}} = D\alpha_c/2$ to account for the adatom interactions, where α_c is *several orders of magnitude less than one* for typical MBE conditions.

Table 1. Comparison of transition temperatures at which step flow occurs, calculated using Monte Carlo simulations [16], nonlinear theory including adatom interactions (7), and the Einstein relation (8). Parameters used are for a GaAs(100) surface with $a = 3.98 \times 10^{-8}$ cm^{-2}, $n_0 = 1/a^2$, $E_D = 1.3$ eV, $\sigma = 1$, $m = 5$, and $\nu = (2k_B T)/h$, where here h is Planck's constant.

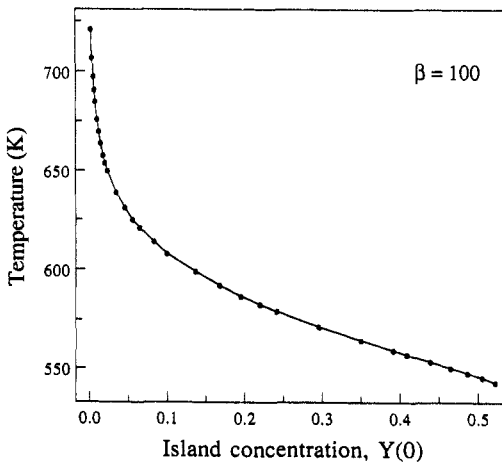|			T_c (K)	
J (cm^{-2} s^{-1})	h/a	Simulation	Theory	Einstein relation
5.0×10^{13}	10	650	654	520
1.0×10^{14}	10	680	673	533
5.0×10^{14}	10	725	722	563
1.0×10^{15}	10	735	746	577
1.0×10^{14}	14	700	707	545
1.0×10^{14}	20	750	750	559
5.0×10^{14}	20	815	811	592
2.3×10^{14}	18	775	766	571

Figure 3. Effect of temperature on the island concentration $2N(x)/n_0 = \alpha Y(x)$ at $x = 0$. Note the sharp dependence of the temperature on $\alpha Y(0)$ for low concentrations. Calculations are done using (5) and (7) for stepped GaAs(100) with $h = 10a$, $n_0 = 1/a^2$, $a = 3.98 \times 10^{-8}$ cm^{-2}, $E_D = 1.3$ eV, $\nu = 2.5 \times 10^{13}$ s^{-1}, $J = 1 \times 10^{14}$ cm^{-2} s^{-1}, $\sigma = 1$ and $m = 5$.
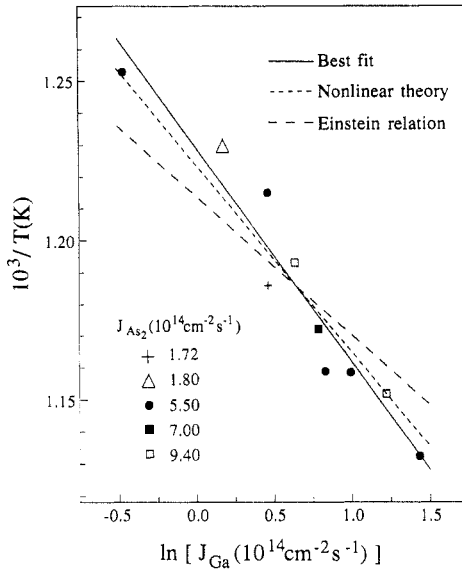
Figure 4. Measurements of T_c for MBE on GaAs(001) for the indicated Ga and As$_2$ fluxes (from [3]). Least-squares fits of (7) to the data are shown with E_D as an adjustable parameter and for α_c also adjustable ('best fit'), α_c given by the nonlinear theory using $Y_0 = 0.01$, and for the Einstein relation. For the 'best fit,' nonlinear, and Einstein theories, the values of α_c are 1.4×10^{-4}, 1.7×10^{-3}, and 2, respectively and the values for E_D are 1.3 eV, 1.4 eV, and 2.0 eV, respectively.

We show in figure 4 values of T_c measured during MBE for GaAs(001) [3] for various Ga and As$_2$ fluxes compared with a least-squares fit of (7), with both E_D and α_c as adjustable parameters, a least-squares fit of (7) with $\alpha_c = 2$ (the Einstein relation), and with α_c calculated at $Y(0) = 0.01$ from our nonlinear theory, in accordance with the results shown in table 1. The correspondence between α_c calculated from our nonlinear theory to the 'best fit' of the data confirms that due to island-formation, step flow-dominated growth is only reached when the diffusion time is several orders of magnitude less than time for the step to move a terrace length. By contrast, attempting to fit the Einstein relation to the measurements requires $E_D = 2.0$ eV, an extremely high value; if a lower, more realistic energy were used (e.g. 1.3–1.4 eV as predicted by the 'best fit' and the nonlinear theory), the Einstein relation would predict T_c several hundred degrees below the measurements (cf table 1), thus highlighting the essential contribution of the nonlinear adatom interaction term in accurate predictions of epitaxial growth regimes.

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