PHYSICAL REVIEW B VOLUME 47, NUMBER 16 15 APRIL 1993-II

Microscopic theory of epitaxial growth on vicinal surfaces

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(Received 10 December 1992)

We formulate a microscopic theory to describe epitaxial growth on vicinal surfaces in the regime where the step velocity can be considered slow and the only island-formation processes involve adatoms and dimers. A solution for the nonlinear equations describing the adatom and dimer concentrations and currents is obtained based on the assumption that Fick's law holds for the adatoms. Our general solution closely resembles that recently obtained from a macroscopic description based on the surface activity with the notable difference that our result includes a dependence on the dimer binding energy. We are also able to more accurately describe the absorbing boundary condition at the steps than is possible with a macroscopic theory.

I. INTRODUCTION

A theoretical understanding of crystal growth by molecular-beam epitaxy requires significant modifications of the basic near-equilibrium step-flow model of Burton, Cabrera, and Frank (BCF).[1] The most dramatic of these results from the incorporation of effects due to the formation and dissolution of islands created on the terraces by adatom interactions. This introduces terms in the kinetic equation describing the adatom concentration including a nonlinear term that makes analytical solution a formidable undertaking. Understandably, existing studies of this equation have until recently employed numerical solutions[2,3] and no analytical solutions of any kind had been reported for the adatom concentration.[4] Thus the exact analytical solution obtained by Luse *et al.*[5] (LZVW) is of very particular interest.

LZVW replace the adatom concentration by a quantity they identify as the surface activity that satisfies a BCF-type kinetic equation. For the case that dimer formation dominates all other island-formation effects, this equation, which is nonlinear in the adatom concentration but linear in the activity, together with the kinetic equation for the dimer concentration allow an exact solution to be obtained for the adatom concentration. Some restrictions apply in addition to the neglect of n-mer effects for $n \geq 3$; the dimers are assumed to be stationary, a restriction present in earlier work also,[2,3] and the velocity of the advancing steps is considered sufficiently slow that the step can be considered as fixed in solving the boundary value problem as is done in the original BCF theory.[1] These restrictions do not alter the nonlinear aspect of the problem and are not expected to affect qualitative conclusions based on the solution obtained.

The underlying theoretical framework used by LZVW, in common with that used in the earlier work cited, is macroscopic and therefore subject to additional restrictions which we have discussed in detail elsewhere.[6] Briefly, the absorbing boundary condition at the steps and the assumption of Fick's law relating adatom concentration and flux are in general problematic and an exact theory would, in our opinion, dispense with the latter and make use of a more physical boundary condition. This requires a microscopic description,[6] which we formulate here. At this time our emphasis will be to complement the result of LZVW and to provide a theoretical platform from which it will be possible to subsequently consider further refinement. Since corrections to Fick's law are expected to be small when adatom desorption is negligible,[6] as is true here,[2(a)] we focus our attention on the case where this relationship holds but the dimers can also be mobile. The main result of this paper is an exact solution for the adatom concentration for this case. Our result is quite similar qualitatively to that obtained by LZVW with the notable exception that our general expression for the adatom concentration includes a dependence on the dimer binding energy E_n, while their result is independent of this quantity. In the appropriate limit this dependence vanishes and our result, like theirs, reduces to the BCF result.

We describe the microscopic formulation and obtain the related equations, which include the nonlinear dimer formation term, in Sec. II. The solution of these equations is discussed in Sec. III at a level of approximation for the microscopic theory that is consistent with the macroscopic theories but also more general than these. In Sec. IV we comment on the case where the adatom concentration and current are independent variables and the dimers are immobile. We then consider the case where Fick's law relates the adatom concentration and current and the dimers are mobile. A discussion of our results follows in Sec. V. In concluding this Introduction we want to emphasize that our primary purpose here is to establish the microscopic formulation as a theoretical framework that complements that used by LZVW and that may also offer advantages relative to treatment of the step boundary condition for absorption and possibly also non-Fickian effects. Both formulations lead to exact solutions for the nonlinear equations describing the adatom concentration when effects due to dimers dominate and appear to be promising candidates for the analytical study of regimes where trimer and larger clusters become significant.

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II. THE MICROSCOPIC FORMULATION

We consider the identical situation studied by LZVW;[5] a flux F is incident on a terrace of length 21; the step velocity is assumed sufficiently slow that the steps terminating the terrace at $\pm l$ can be considered stationary. The range of temperature and deposition rates allowable is such that only adatoms and dimers need to be taken into account. Then if $f(x,v)$ and $\mathcal{F}(x,V)$ are the distribution functions in position-velocity space for adatoms and dimers on the terrace, $-l \le x \ge l$, in the steady state these quantities satisfy kinetic equations of the form

$$v\frac{\partial f}{\partial x}=\omega(f)+\omega^1(f,\mathcal{F})+\frac{Fe^{-(v^2/2kT)}}{(2\pi kT)^{1/2}} , \tag{1a}$$

$$V\frac{\partial f}{\partial x}=\Omega(\mathcal{F})+\Omega^1(f,\mathcal{F}) . \tag{1b}$$

Here v and V are velocities of adatoms and dimers moving on the terrace, $\omega(f)$ and $\Omega(\mathcal{F})$ describe the changes in f and $\mathcal{F}$ due to the random forces acting on them, and ω^1 and Ω^1 the changes due to coalescence, dissolution and, in the case of ω^1, reduction of the beam flux due to impingement of a beam adatom adjacent to an occupied site. The surface parameters are the number of nearest neighbors, $m=4$, and site density, a^{-2}; also, σ is the capture number, τ and τ_0 are characteristic times describing the deposition rate and adatom surface diffusion, and the mass units are taken so that the adatom mass is unity. Then we have[6]

$$\omega(f)=\zeta\left[kT\frac{\partial^2}{\partial v^2}+1+v\frac{\partial}{\partial v}\right]f , \tag{2a}$$

$$\Omega(\mathcal{F})=\zeta^*\left[kT\frac{\partial^2}{\partial V^2}+1+V\frac{\partial}{\partial V}\right]\mathcal{F} , \tag{2b}$$

where the friction coefficients ζ and ζ^* are related to the surface diffusivities by Einstein's relation, e.g., $\zeta/kT=D^{-1}$. Note that $\zeta=\tau_0^{-1}$; we will not need to estimate ζ^* in what follows.

The terms ω^1 and Ω^1 can be determined in much the same way related terms are for the macroscopic theory.[2,3] Consider first ω^1, which contains a beam reduction term

$$\omega_B^1=-4\tau^{-1}\int dv\, f(x,v) \tag{3a}$$

that has no counterpart in Ω^1. The remaining part of ω^1, accounting for gain (or loss) of adatoms, has a counterpart in Ω^1 accounting for the corresponding loss (or gain) due to dissolution (or coalescence). In an obvious notation,

$$\omega_C^1=-2\sigma a^2\tau_0^{-1}f(x,v)\int dv^1 f(x,v^1)-4\tau^{-1}Ff(x,v) , \tag{3b}$$

where the factor 2 in the first term occurs since either colliding partner could be lost. The first term accounts for losses due to coalescence while the second accounts for losses due to a beam particle occupying one of the $m=4$ adjacent sites. Similarly,

$$\Omega_D^1=\tau_0^{-1}e^{-E_n/kT}\mathcal{F}(x,V) . \tag{4}$$

To complete our specifications we need to identify ω_D^1 and Ω_C^1, i.e., the gain terms in each equation. This is neither simple nor, fortunately, necessary as will be explained in the next section. Consider, e.g., ω_D^1, which is the counterpart of Ω_D^1. Dissolution of a dimer may or may not produce an adatom with velocity v leading to a contribution to ω_D^1. Similarly, the coalescence events included in ω_C^1, Eq. (3), may or may not produce a dimer with velocity V, i.e., at the microscopic level of description we need to specify the velocity of the product species requiring terms involving integrals containing δ functions ensuring conservation of momentum and energy. We will not need to solve Eqs. (1) directly since our interest is in determining the concentrations and currents, $n(x)$, $j(x)$ and $N(x)$, $J(x)$, which are defined as

$$n(x)=\int dv\, f(x,v),\quad j(x)=\int dv\, v\, f(x,v) , \tag{5}$$

$$N(x)=\int dV\, \mathcal{F}(x,V),\quad J(x)=\int dV\, V\, \mathcal{F}(x,V) , \tag{6}$$

and, as will be shown in the next section, Eqs. (1)–(4) already contain all the ingredients necessary to obtain these quantities by standard methods.[6] In concluding this section we note that in writing the first term in Eq. (3) using the single relaxation time τ_0 we have made an approximation. The actual relaxation time would be a function of the relative velocity of the coalescing adatoms and appear inside the integral. Replacing this by an average as we have done should not result in qualitative differences in the equations satisfied by the concentrations and currents based on comparison with extensive experience from the kinetic theory of gases where a similar procedure is used in obtaining the single relaxation time Bhatnager, Gross, and Krook (BGK) equation.[7]

III. MOMENT EQUATIONS

The moments of f and $\mathcal{F}$ are defined as

$$m_i(x)=\int dv\, v^i f(x,v),\quad M_i(x)=\int dV\, V^i\mathcal{F}(x,V) \tag{7}$$

so that, e.g., $m_0=n$, $m_1=j$. Equations for the moments can be obtained from Eq. (1a) [and Eq. (1b)] by multiplying by v^i (and V^i) and integrating over v (V). For $i=0$ we then obtain

$$\frac{dm_1}{dx}=F-\frac{8m_0}{\tau}-\frac{2\sigma a^2}{\tau_0}m_0^2+\int dv\,\omega_D^1 , \tag{8a}$$

$$\frac{dM_1}{dx}=\int dV\,\Omega_C^1-\frac{e^{-E_n/kT}}{\tau_0}M_0 . \tag{8b}$$

Equations (8) are the steady-state concentration conservation equations. Since two adatoms are created by each dissolution event, and conversely one dimer is created by each coalescence event that reduces the adatom population by two, the integral term in Eqs. (8) can be determined by comparison with their counterpart terms which are explicit, and we have

$$\frac{dm_1}{dx}=F-\frac{8m_0}{\tau}-\frac{2\sigma a^2}{\tau_0}m_0^2+\frac{2}{\tau_0}e^{-E_n/kT}M_0\ , \tag{9a}$$

$$\frac{dM_1}{dx}=\frac{4m_0}{\tau}+\sigma\frac{a^2}{\tau_0}m_0^2-\frac{M_0}{\tau_0}e^{-E_n/kT}\ . \tag{9b}$$

The right-hand sides of Eqs. (9) are identical with the corresponding terms appearing in the conservation equations used in previous work[2,3] and, if Fick's law were assumed Eq. (9a) would reduce to the generalized BCF equation studied in Ref. 2(a) [Eq. (10) there]; note that our equation has no convective term resulting from fast step motion and in Ref. 2(a) no dissolution effects are considered. Similarly, if M_1 is set equal to zero, i.e., the dimers are assumed to be immobile, then Eq. (9b) is identical in the steady state to the equation used by LZVW (Ref. 5) [their Eq. (14)] and also in Ref. 2(a) [Eq. (18) there] without the coalescence term. At this point our equations are more general with the concentrations and currents being independent variables. However, we also have more unknowns than equations.

Another set of equations can be obtained by multiplying Eq. (1a) by v, Eq. (1b) by $2V$, and integrating over the appropriate velocity. These equations describe the steady-state changes in momentum current (hence the $2V$ instead of V). We only require the first of these here,

$$\frac{dm_2}{dx}+\zeta m_1=\frac{-4m_1}{\tau}-\frac{2\sigma a^2}{\tau_0}m_0m_1+\frac{2}{\tau_0}\beta e^{-E_n/kT}M_1\ , \tag{10}$$

where the last term on the right-hand side is again determined by comparison with its counterpart term from Eq. (1b). The factor $\beta\leq 1$ is included here for completeness but in what follows we set it equal to 1. This allows for the possibility that as a result of dissolution a dimer may transfer some of its momentum to the substrate lattice; since we are unable to assess this effect here we assume that $\beta=1$ and all such interaction is included in the Ω term.

In principle additional moment equations involving higher-order moments, $i\geq 2$, could be written. The number of such equations necessary to consider will depend on the level of approximation used to determine the distribution functions f and $\mathcal{F}$. Here we consider the level of approximation consistent with the conventional macroscopic description. It should be emphasized though that consistency is not necessarily equivalence since at any level of approximation we retain the ability to more precisely prescribe boundary conditions and to describe possible effects due to non-Fickian diffusion.

In the next section we consider Eqs. (9) and (10) for two cases in which m_1 or M_1 are made dependent variables. This will still leave us with three equations and four unknowns (e.g., m_0, m_1, m_2, M_0 with M_1 specified); there is thus a closure problem that additional moment equations cannot remedy. The standard[7] procedure for effecting closure is to expand f (and $\mathcal{F}$) in terms of its moments and retain a finite number of terms; a two-term expansion here is consistent with the macroscopic description. Because of the geometry we are considering a half-range expansion is most convenient and accordingly we require

$$f(x,v)=f_i(x,v)=n_i(x)\frac{e^{-v^2/2kT}}{(2\pi kT)^{1/2}}\ ,$$
$$i=1,\ v>0;\ i=2,\ v<0\ , \tag{11a}$$

$$\mathcal{F}(x,V)=\mathcal{F}_i(x,V)=N_i(x)\frac{e^{-V^2/kT}}{(\pi kT)^{1/2}}\ ,$$
$$i=1,\ V>0;\ i=2,\ V<0\ . \tag{11b}$$

This allows us to eliminate m_2 in Eq. (10),

$$m_2=\int dv\, v^2 f(x,v)=\alpha m_0,\quad \alpha=kT\ . \tag{12}$$

We also note for future reference that

$$m_0=\tfrac{1}{2}(n_1+n_2),\quad m_1=\left[\frac{\alpha}{2\pi}\right]^{1/2}(n_1-n_2)\ . \tag{13}$$

With Eqs. (9), (10), (12), and (13) with the related expressions for M_0, M_1 we can dispense with further consideration of f and $\mathcal{F}$ and focus our attention on determining the moments which are the quantities of interest.

IV. SOLUTIONS

A. BCF limit

It will prove useful for comparison with the results of LZVW to incorporate the most general solution for the case where there are no dimer effects into our results. This will be referred to as the BCF solution and it represents a limiting case for the results we obtain in Sec. IV C. From Eqs. (9a) and (10), with Eq. (12) and the Einstein relationship $D=\alpha/\zeta$ we have

$$n(x)=B-\frac{fx^2}{2D},\quad j(x)=-Dn'(x)=Fx\ , \tag{14}$$

where the symmetry condition has been used to reduce the number of constants determined by the boundary conditions to just B. Note that as we discussed earlier, the approximation embodied by Eqs. (11) is consistent with the macroscopic description and Fick's law holds. To show that this description is not necessarily equivalent to the macroscopic description we consider the case of an absorbing step as treated in Refs. 2(a) and 5. In the macroscopic description this condition is specified by the unphysical requirement that $n(-l)=n(l)=0$. The macroscopic description does not allow discrimination between incident and exiting adatoms at the step but in the microscopic theory this is possible and we can specify $n_1(-l)=n_2(l)=0$ resulting in a different value for the constant B and a nonvanishing step concentration. Specifically, for the macroscopic boundary condition

$$B_{\text{mac}}=\frac{l^2F}{2D}\ , \tag{15}$$

whereas the true absorbing boundary condition follows from Eq. (13) as

$$B = B_{\text{mac}} - Fl\left[\frac{\pi}{2\alpha}\right]^{1/2} \tag{16}$$

so that $a^2 B$ is typically reduced by about 5–10% since $B_{\text{mac}} \propto (1/a)^2$ and the correction term, $B \propto (\tau_0/\tau)(l/a)$.

B. Immobile dimers

The equations we have derived allow for the possibility of dimer motion on the terrace. Since a common feature of the earlier work cited[2,3,5] is that all islands are immobile, we begin by briefly discussing Eqs. (9) and (10) for this special case. We naively introduce this approximation into our theoretical framework by replacing Eq. (11b) with

$$\mathcal{F}(x,V) = N(x)\delta(V) \tag{17}$$

so that $M_0 = N$ and identically $M_1 = 0$. This leads to the nonphysical conclusion $m_1 = Fx$ from Eqs. (9) that results from setting $M_1 = 0$ without accounting for the role of the dimers in mediating the transfer of momentum current between the adatoms and substrate. An extended formulation considering a mobile dimer precursor species would be required to properly describe this situation. However, as long as we can proceed with the dimer friction coefficient unspecified we can in effect treat the case of immobile dimers in the context of our original approximation, Eq. (11b). Our primary concern and results will therefore be for the case considered next where the dimers are mobile.

C. Fickian adatoms and mobile dimers

We now return to our original, general formulation, with $\mathcal{F}$ given by Eq. (11b), but impose the condition that the adatom concentration and current are related by Fick's law. A rigorous justification of this assumption would require a perturbation analysis of Eqs. (9), (10), and the counterpart equation for the latter. However, our earlier results[6] in the BCF limit indicate that in the context of Eqs. (11) this assumption is well motivated. The distinction between using Fick's law as an assumption rather than a necessary part of the theoretical framework still remains as one of the features that separates our approach from the macroscopic description used in previous work.[2–5]

With Eq. (12) and Fick's law, Eq. (10) provides us with the relationship

$$\frac{e^{-E_n/kT}}{\tau_0} M_1 = \frac{2m_1}{\tau} + \frac{\sigma}{\tau_0} a^2 m_0 m_1 \ , \tag{18}$$

which we can differentiate and use with Eqs. (9a) and (9b) to obtain

$$\frac{2}{\tau}\frac{dm_1}{dx} + \frac{\sigma a^2}{\tau_0}\frac{\partial}{\partial x} m_0 m_1 = \frac{-e^{-E_n/kT}}{2\tau_0}\left[\frac{\partial m_1}{\partial x} - F\right] \tag{19}$$

or

$$\frac{2}{\tau} m_1 + \frac{\tau a^2}{\tau_0} m_0 m_1 = \frac{-e^{-E_n/kT}}{2\tau_0}[m_1 - Fx] \ , \tag{20}$$

where the constant of integration must be zero since $m_1(x) = m_1(-x)$. If we use Fick's law to replace m_1 in Eq. (20) we can again integrate, obtaining

$$m_0^2 + m_0\left[4\frac{\tau_0}{\tau\sigma a^2} + \frac{e^{-E_n/kT}}{\sigma a^2}\right] + \frac{\zeta e^{-E_n/kT}}{2a^2\sigma\alpha} Fx^2 - A \tag{21}$$

and finally

$$m_0 = -\frac{1}{2}\left[\frac{4\tau_0}{\tau\sigma a^2} + \frac{e^{E_n/kT}}{a^2\sigma}\right] + \frac{1}{2}\left[\left[4\frac{\tau_0}{\tau\sigma a^2} + \frac{e^{-E_n/kT}}{\sigma a^2}\right]^2 - \frac{2\zeta}{\alpha}\frac{e^{-E_n/kT}}{\sigma a^2} Fx^2 + A\right]^{1/2} . \tag{22}$$

Equation (22) has a close similarity to the general result obtained by LZVW;[5] cf. their Eq. (18). The most striking difference is that by allowing dimer mobility on the terraces we retain a dependence on the binding energy E_n in our result. This dependence is absent in the LZVW result, and these authors comment that this "...may appear odd..." and is a consequence of the approximation they used. Our result indicates that the specific cause of this is the neglect of dimer mobility. Note that our result is independent of ζ^*, the dimer friction coefficient, and so the dimer current is not specified and could be vanishingly small. Equation (22) is the main result of this paper.

V. DISCUSSION

First consider the limiting form of Eq. (22) in the BCF limit where $\tau_0/\tau \ll (\tau_0/\tau)(l/a)^2 \ll 1$. We find

$$2\sigma a^2 m_0 \to 2\sigma a^2\left[B - \frac{\zeta}{2\alpha}Fx^2\right]\left[1 + O\left[\frac{\tau_0}{\tau}\frac{l^2}{a^2}e^{-2E_n/kT}\right]\right] \tag{23}$$

and since $e^{-E_n/kT} \ll 1$ we see that the correct general limiting form is directly obtained. The condition on the binding energy will generally be satisfied, but this should be formally included as part of the condition for the BCF limit.

Our primary purpose here has been to establish a theoretical platform to provide the basis for further study that will include effects due to fast step velocity, n-mer islands for $n \geq 3$, and a higher-order approximation than that provided by Eqs. (11). The results we have obtained here indicate that the model considered in Sec. IV C, Fickian adatoms and mobile dimers, provides a description similar to current macroscopic theories. Including island mobility does not appear to affect the quantitative conclusions that follow from this result if $e^{-E_n/kT} \ll 1$ so this may not be a critical issue for current applications [e.g.,[8] $E_n \propto 0.25$ eV for growth on vicinal GaAs (001)].

The result obtained in Sec. IV C is almost identical to that found by LZVW.[5] From Eq. (23) we see that in terms of $\delta = (l^2/a^2)\tau_0/\tau$ our result for the adatom concentration is identical to theirs for the small δ regime for which both theories are valid when δ in our equation is replaced by $\delta' = e^{-2E_n/kT}\delta$. Thus our results lead to the same conclusions as those authors have drawn and, further, we expect that these results will be valid for larger values of beam flux F than might be expected from their result.

In conclusion, we have formulated a microscopic description for epitaxial growth on vicinal surfaces subject to the restriction of slow step velocity and neglect of processes involving n-mer islands for $n \geq 3$. A solution was obtained for the case where the dimers were allowed to be mobile but the adatoms were constrained by Fick's law that closely resembles the result obtained by LZVW (Ref. 5) using a macroscopic theory based on the surface activity. Our result includes a dependence on the dimer binding energy which is not present in their results.

ACKNOWLEDGMENTS

I gratefully acknowledge support from SUNY Stony Brook in the form of a research leave and also acknowledge the hospitality and stimulating environment provided by the Department of Civil Engineering and Operations Research at Princeton University.

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