

Determination of surface-diffusion kinetics of adatoms in epitaxy under step-flow growth conditions

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In an analytical and Monte Carlo simulation analysis of an interrupted step-flow growth on a vicinal substrate, we find that the asymptotic behavior of the adatom monomer density during recovery is dominated by a single exponential decay, $\exp(-\pi^2 Dt/4L_{\text{terrace}}^2)$. Here D is the adatom diffusion coefficient over flat terraces, and L_{terrace} is the averaged width of the terraces. Consequently, by monitoring the recovery of optical reflectance difference or reflection high-energy electron diffraction from such a surface, one should be able to determine reliably the adatom diffusion coefficient under high-temperature growth conditions.

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Vapor-phase homoepitaxy and heteroepitaxy have become two of the main growth techniques for fabricating new materials used in optoelectronics, magnetic recording and storage, and microelectronics. Most of these new materials are grown at high temperatures. This is necessary because at high rates of deposition and growth, overlayer atoms or molecules need to have enough mobility to reach the edges of terraces or two-dimensional islands to form flat films with atomically sharp interfaces. One of the crucial parameters that determine the growth mode and in turn the quality of an epitaxially grown material is the surface-diffusion coefficient of overlayer adatoms or molecules. There are few reliable techniques that can be used to measure such a parameter at or close to the growth temperature of approximately 700 K.

By monitoring the transition temperature from a two-dimensional (2D) growth (through nucleation and growth and coalescence of 2D islands) to a step-flow growth, Neave and coworkers suggested an indirect way to determine the surface-diffusion coefficient of Ga on As-terminated GaAs(100) at approximately 590 °C.¹ The essence of the proposition given by Neave *et al.* is the following: the disappearance of reflection high-energy electron diffraction (RHEED) oscillation during continuous growth as the substrate temperature increases, signifies that the diffusion length of adatoms or molecules equals or exceeds the widths of the terraces. Knowing the terrace width and the deposition rate, such a proposition enables one to determine the surface-diffusion coefficient. Recently, Kajikawa *et al.* further refined the original analysis of Neave *et al.* to include more complicated kinetics situations.² However, it is not clear that the disappearance of RHEED *quantitatively* occurs when the diffusion length equals the terrace width, and thus a reliable determination of surface-diffusion coefficients requires a much more involved analysis of the transition from 2D growth to step-flow growth.^{2,3,4}

Recently, a number of novel techniques have been developed and shown to be effective in determining surface-diffusion kinetics parameters. One of these techniques is the scanning tunneling microscopic (STM) measurement of island density N at a constant deposition flux and different temperatures, or vice versa.⁵ By invoking the nucleation theory,⁶ one finds $N \sim \exp(-E_{\text{diff}}/\gamma k_B T)$ where the factor γ is known once the critical island size is known. Unfortu-

nately, the STM measurement of this type is typically carried out at below 160 K rather than at 700–900 K where the step-flow growth occurs. It is not obvious that the kinetics parameters obtained at such low temperatures apply at high temperatures, given the complexity of the morphology on a growth surface.

Another method is the optical diffraction technique developed by Zhu and coworkers.⁷ In this case, a periodic density distribution of adatoms or molecules is prepared on a substrate with either the method of laser-induced desorption or atomic beam channeling through a laser standing wave, and the linear diffraction of a probe laser beam from such a distribution is monitored.^{7,8,9} From the decay of the optical diffraction signal, one can directly extract the surface-diffusion coefficient of adatoms. The optical diffraction measurement is usually performed at temperatures much closer to the temperature of step-flow growth. There have been numerous reports of surface-diffusion studies using this optical diffraction technique.^{7,10,11} The implementation of such an optical diffraction method, however, is still fairly involved at the present time, and it remains to be shown that it can yield surface-diffusion kinetics parameters in time to meet the needs of material epitaxy. It is desirable to explore other simpler and more direct experimental methods to measure surface-diffusion kinetics of adatoms under growth conditions. This is the subject of this paper.

Consider an interrupted deposition and growth cycle in a step-flow growth regime.^{12,13} The terraces on a vicinal substrate are covered mostly with adatom monomers since nucleation and 2D island growth are suppressed. During the deposition part of the cycle, the monomer density increases at a rate proportional to the deposition flux. The equilibrium density of the monomers is determined by the diffusion-limited growth at terrace edges and the deposition flux. During the growth or recovery part of the cycle, the deposition is stopped and the monomer density decreases as the adatoms diffuse towards the terrace edges and become attached. Assume that there are no significant desorption of adatoms, the total number of adatoms on the growth surface remains unchanged except that the number of adatoms incorporated within the terraces increases quantitatively at the expense of adatom monomers. We next show that under a rather general condition, the asymptotic behavior of such a decay is single

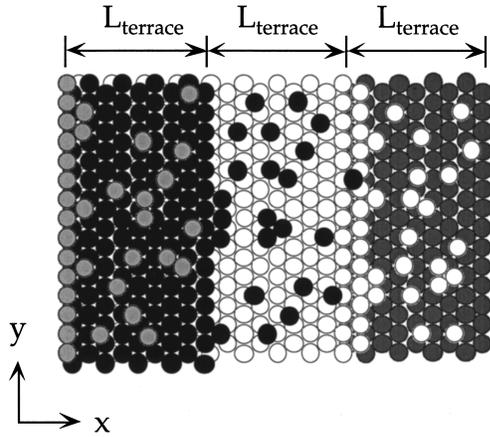


FIG. 1. A sketch of a model vicinal substrate surface with a square lattice during a step-flow epitaxy. The widths of the terraces are roughly constant and determined by the miscut angle.

exponential and the exponent is proportional to the surface-diffusion coefficient of the adatoms.

The decay of the adatom monomer density can be monitored with either the specular reflection of high-energy electron diffraction (RHEED), or more simply, optical reflectance difference techniques.^{12–18} For example, the optical reflectance difference from such a surface measures the difference of the optical response of incorporated terrace adatoms and adatom monomers, and is thus directly proportional to the adatom monomer density. By monitoring the optical reflectance difference during the recovery part of the interrupted step-flow growth, we directly monitor the decay of the adatom monomer density.¹³ By performing measurements on differently miscut substrates, we can also determine the sticking probability of adatoms at the terrace edges from such a simple measurement. A preliminary experiment using such a concept has been reported recently by Zhu and coworkers.¹³ One can also use the intensities of the specular reflection or higher-order diffractions in a RHEED measurement to monitor the recovery of the adatom monomer density. These intensities are also expected to be proportional to the monomer density under step-flow growth conditions when the adatoms on terraces are mostly in the form of monomers.

We now study the evolution of the adatom monomer density after the deposition is interrupted. *In a step-flow growth regime, the edges of terraces advance while the averaged terrace width L_{terrace} remains unchanged at all times.* We treat L_{terrace} as a constant for a given vicinal substrate. Let the x axis be perpendicular to and the y axis be along the averaged step edge. In the coordinate frame that moves with an advancing step edge, the terrace with a constant width L_{terrace} remains stationary. In Fig. 1, we show a sketch of a model vicinal surface with adatoms on the terraces during step-flow growth. The motion of adatom monomers is governed by Fick's law. Since both Fick's law and the mass conservation are satisfied locally rather than globally, *the diffusion equation is expected to be satisfied in the coordinate frame riding with the moving step edge.* This observation is confirmed by our Monte Carlo simulation of a lattice gas as we will describe shortly.

As a result, the evolution of the adatom monomer density

on a terrace in the moving frame is described by the one-dimensional diffusion equation,

$$\frac{\partial \theta}{\partial t} = D \frac{\partial^2 \theta}{\partial x^2}. \quad (1)$$

Let $x=0$ be at the edge of the upper terrace, and $x=L_{\text{terrace}}$ be at the edge of the lower terrace. We assume that the Schwoebel-Erlich barrier at the edge of the lower terrace is large enough that at the growth temperature there is no interlayer transport. Therefore, the boundary condition at $x=L_{\text{terrace}}$ is given by

$$\left. \frac{1}{\theta} \frac{\partial \theta}{\partial x} \right|_{x=L_{\text{terrace}}} = -\frac{1}{4} \left. \frac{\partial \theta}{\partial x} \right|_{x=0}. \quad (2a)$$

Such a nonlinear boundary condition is the result of the fact that the edge of the lower terrace advances during the step-flow growth and thus makes room for adatoms on the interrogated terrace. At low coverage, as is case in the asymptotic limit of the recovery, Eq. (2a) is approximated by

$$\left. \frac{\partial \theta}{\partial x} \right|_{x=L_{\text{terrace}}} \approx 0. \quad (2b)$$

It is not difficult to extend the present analysis and the subsequent Monte Carlo simulation to cases where there is significant interlayer transport. At $x=0$, if we assume that once an adatom strikes the step edge it becomes attached, namely the sticking probability $s=1$, the boundary condition is given by

$$\theta=0. \quad (3a)$$

If the sticking probability s is less than 1, the proper boundary condition at $x=0$ is modified as

$$\frac{\partial \theta}{\partial x} = \left(\frac{s}{a_l} \right) \theta, \quad (3b)$$

where a_l is the surface lattice constant.

We first consider the case when the sticking probability $s=1$ or is close to 1. In the limit of low coverage ($\theta \leq 0.5$), the diffusion equation with the boundary conditions given by Eqs. (2b) and (3a) is approximately solved by

$$\begin{aligned} \theta(x,t) = & \sum_{n=1} \theta_{n0} \sin \left[\left(n - \frac{1}{2} \right) \pi \frac{x}{L_{\text{terrace}}} \right] \\ & \times \exp \left[- \left(n - \frac{1}{2} \right)^2 \frac{\pi^2 D}{L_{\text{terrace}}^2} t \right]. \end{aligned} \quad (4)$$

θ_{n0} 's are determined from the initial condition immediately after the deposition. Most importantly, the asymptotic behavior of the adatom monomer density during recovery is dominated by

$$\begin{aligned} \theta_1(x,t) = & \theta_{10} \sin \left(\frac{\pi}{2} \frac{x}{L_{\text{terrace}}} \right) \exp \left(- \frac{\pi^2 D}{4L_{\text{terrace}}^2} t \right) \\ & \sim \exp \left(- \frac{\pi^2 D}{4L_{\text{terrace}}^2} t \right). \end{aligned} \quad (5)$$

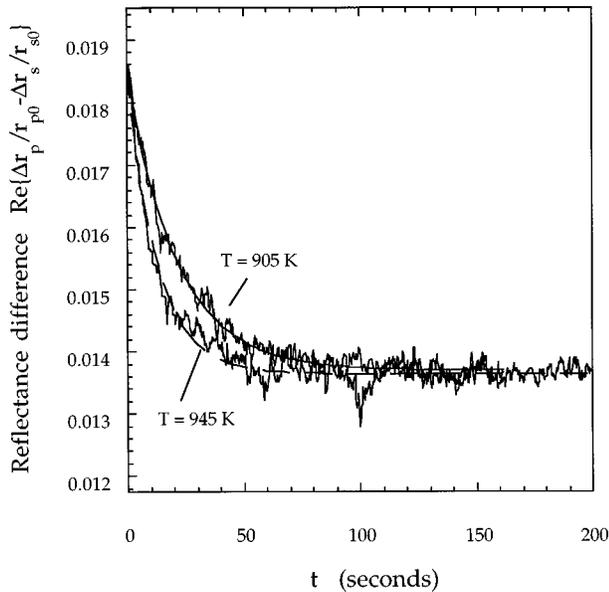


FIG. 2. Polarization-modulated reflectance difference signals from SrTiO₃(001) during the recovery of an interrupted growth of SrTiO₃ at two different temperatures. At $T = 905$ K, the decay exponent is $\alpha = 0.047 \text{ sec}^{-1}$. At 945 K, $\alpha = 0.09 \text{ sec}^{-1}$. The diffusion barrier is found to be 1.2 eV/atom .

As we mentioned earlier, the optical polarization-modulated reflectance difference signal $I(t)$ at *oblique incidence* from such a vicinal surface is proportional to the density of the adatom monomers multiplied by the difference of the optical polarizability of an adatom monomer and an incorporated adatom on the substrate.^{13,19,20} Consequently, the asymptotic decay of $I(t)$ is also proportional to $\theta_1(x, t) \sim \exp(-at) \sim \exp(-\pi^2 Dt/4L_{\text{terrace}}^2)$. From the decay exponent α of the optical reflectance signal, we easily extract the surface-diffusion coefficient D at the growth temperature. In Fig. 2 we show the optical reflectance difference signal from a vicinal SrTiO₃(001) during the recovery of an interrupted homoepitaxy. The decay of the optical signal is well described with a single exponential function, as given by Eq. (5).¹³

If the sticking coefficient s is significantly smaller than one, the solution to Eq. (1) is then subject to the boundary conditions of Eqs. (2b) and (3b). The decay exponent α satisfies the following equation:

$$\cot\left(\sqrt{\frac{\alpha}{D}} L_{\text{terrace}}\right) = \frac{a_1}{sL_{\text{terrace}}}\left(\sqrt{\frac{\alpha}{D}} L_{\text{terrace}}\right). \quad (6)$$

Since $\sqrt{\alpha/D} \sim 1/L_{\text{terrace}}$, Eq. (6) reduces to $\cot(\sqrt{\alpha/D} L_{\text{terrace}}) \approx 0$ when $s \sim 1$ and we recover Eq. (4). In general, we can determine the decay exponent α as a function of averaged terrace width L_{terrace} at a fixed temperature by performing the measurement on two samples with different miscut angles and in turn different terrace widths. From Eq. (6) together with the two measured decay exponents and the two corresponding terraces widths, we have two equations for two unknowns: D and s . In this way, we can determine both the surface-diffusion kinetics parameter D and the sticking probability s .

To further substantiate the above analysis, we have performed a Monte Carlo simulation of an interrupted step-flow

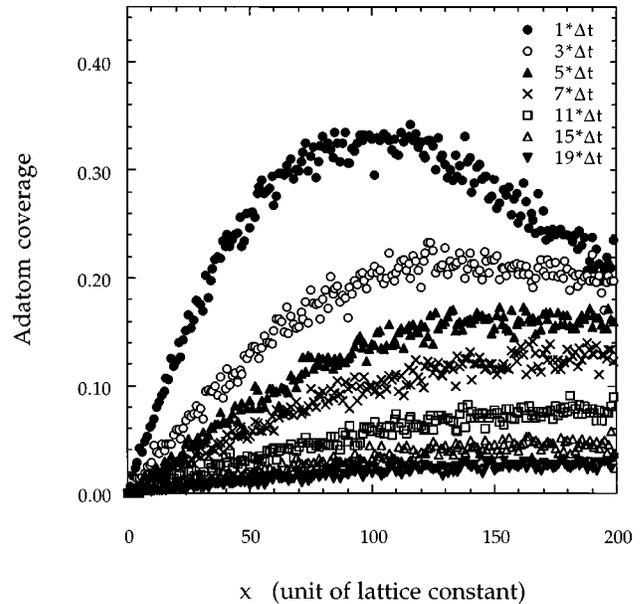


FIG. 3. Adatom coverage profiles versus recovery time $t = N\Delta t$ with $\Delta t = 8000\tau_{\text{residence}}$ (see text) on a vicinal substrate of square lattice as shown in Fig. 1. The averaged width of terraces L_{terrace} is 200 times that of lattice constant a . The surface-diffusion coefficient of an adatom is given by $D = a^2/4\tau_{\text{residence}}$.

growth of a noninteracting lattice gas on a square lattice with $400 a_1$ along the x axis, and $2000 a_1$ along the y axis, as similarly sketched in Fig. 1. To simulate a vicinal surface, we make the first column of the lattice the initial upper terrace edge, the next 200 columns the terrace under interrogation so that the terrace width is $L_{\text{terrace}} = 200 a_1$, and the remaining 199 columns the lower terrace. Initially, we randomly deposit adatoms on the terrace of interest to a coverage of 0.5. We subsequently allow adatoms to perform random walk. In our simulation, we assume that (1) adatoms cannot descend to the lower terrace as a result of the Schwoebel-Erlich barrier; (2) adatoms can not ascend to the upper terrace; (3) the sticking coefficient of adatoms reaching the edge of the upper terrace is unity, $s = 1$; (4) the diffusion rate of adatoms along the step edge is fast compared to the growth rate of the terrace, such that an atom at the step edge always diffuses to and settles down at a site with the maximum possible bond coordination. To take the effect of step flow into consideration in the mean field sense, once an adatom becomes attached and settles down at a stable site at the edge of the upper terrace, we make the lattice site on the lower terrace with its x coordinate $L_{\text{terrace}} = 200 a_1$ from this site the new terrace edge. This procedure computationally leads to the flow of the step edge as a result of growth. At low coverage and high temperature, when there is negligible 2D island formation, it is sufficient to treat adatoms as noninteracting lattice gas.

We record the adatom monomer density or coverage profile after each time interval where $\Delta t = 0.2\tau_{\text{residence}} \times (L_{\text{terrace}}/a_1)^2 = 8000\tau_{\text{residence}}$. $\tau_{\text{residence}}$ is the residence time of an adatom at an isolated site on an open terrace. The tracer diffusion rate of such an atom is given by $D = a_1^2/4\tau_{\text{residence}}$. In Fig. 3, we display the evolution of the adatom monomer density profile in the coordinate frame that moves with the advancing step edge. After a time of $7\Delta t$

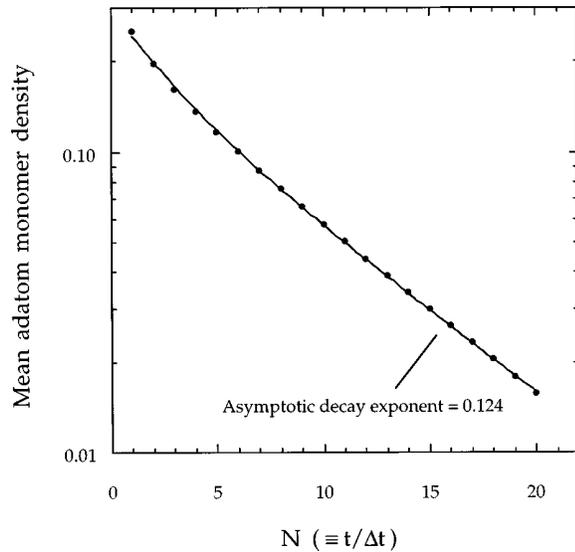


FIG. 4. Spatially averaged adatom monomer density (solid circles) versus normalized time $N = t/\Delta t$. The solid line is a fit to a double exponential function $f(N) = A_1 \exp(-\alpha_1 N) + A_2 \exp(-\alpha_2 N)$. We find $\alpha_1 = 0.124$ and $\alpha_2 = 3\alpha_1$.

$= 56000\tau_{\text{residence}}$, the profile is well described by Eq. (5). By fitting the spatially averaged density versus time to a double exponential function, as shown in Fig. 4, we find that the slow decay component varies with time $t = N\Delta t$ as $\exp(-\alpha_1 N) = \exp(-0.124N)$. The exponent 0.124 agrees within 1% with the theoretical value of $\pi^2 D \Delta t / 4L_{\text{terrace}}^2 = 0.2(\pi/4)^2 = 0.1234$ from Eq. (5). The fast decay component has an exponent α_2 3 times as large as α_1 , as expected from Eq. (4). The excellent agreement between the Monte Carlo simulation and our earlier analytical analysis confirms the assumptions of Eq. (1) and the associated boundary condition.

We now discuss the limitations of the proposed method and how they may be overcome. In our present investigation, we have assumed that there is negligible 2D nucleation and

most adatoms on terraces are in the form of monomers. This assumption is reasonable since in the step-flow growth regime where the substrate temperature is generally high, 2D islands are expected to be unstable and adatoms behave approximately as an assemble of noninteracting monomers. In cases when there is a substantial nucleation, we will need to invoke the appropriate nucleation theory to separate the effect of nucleation and dissociation of 2D islands from the effect of monomer diffusion on the recovery of the optical reflection or RHEED signals. This is the subject of our further investigation. We have also assumed that adatoms do not descend from an upper terrace to a lower terrace as a result of a significant step edge barrier E_{step} . For a finite E_{step} , we will need to modify Eq. (2b) as follows: $\partial\theta/\partial x|_{x=L_{\text{terrace}}} \approx [\exp(-E_{\text{step}}/k_B T)/a_l] \theta|_{x=L_{\text{terrace}}}$. If $a_l \exp(E_{\text{step}}/k_B T) \gg L_{\text{terrace}}$, Eq. (4) and Eq. (5) remain valid. In the limit that $a_l \exp(E_{\text{step}}/k_B T) \ll L_{\text{terrace}}$, Eq. (5) is changed to $\theta_1(x, t) \sim \exp(-\pi^2 D t / L_{\text{terrace}}^2)$. A more detailed analysis may enable us to determine E_{step} as well as D and s . Furthermore, we have assumed that the diffusion rate along a step edge is fast compared to the growth rate so that the step edge remains straight and parallel to neighboring step edges. Our method fails if the growth at the step edges is of dendritic form due to lack of mobility along the step edge. In this case, the average width of the terraces is ill-defined and the recovery of the optical or RHEED monitor is no longer related to the surface-diffusion kinetics in a simple way.

In conclusion, we have shown a simple and reliable method of measuring the surface-diffusion coefficient D on terraces and stick probability s at step edges of adatoms or molecular adsorbates under the epitaxial step-flow growth condition at high temperature. Such a method is easily implemented in most epitaxial growth systems.

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