

Atomic-Scale Mechanisms for Surfactant-Mediated Layer-by-Layer Growth in Homoepitaxy

Zhenyu Zhang and Max G. Lagally

University of Wisconsin, Madison, Wisconsin 53706

(Received 14 October 1993)

Atomic-scale mechanisms for surfactant-mediated layer-by-layer growth in homoepitaxy are investigated theoretically. Starting with minimal assumptions on relative bond strengths, we demonstrate that four possible mechanisms can be operative in enhancing layered growth: (1) a high density of islands at the initial growth stage of each layer, (2) a reduced activation barrier for atoms to cross steps, (3) incorporation into a growing island, and (4) an effective increase in the migration rate on top of the island. We assess the relative importance of these processes by computer simulations.

PACS numbers: 68.55.Bd, 68.35.Bs

Over the last few years, there has been an increasing interest in surfactant-mediated layer-by-layer growth for both semiconductor and metal systems in heteroepitaxy and homoepitaxy [1-10]. In these studies, the term "surfactant" refers to a monolayer or a submonolayer of foreign atoms on the surface. The classical definition of surfactant is "a substance that lowers surface tension, thereby increasing spreading and wetting properties" [11]. Indeed, it has been observed that the preadsorption of suitable surfactants such as As, Sb, and Te can change the mode of Ge growth on Si(100) from 3D cluster growth to layer-by-layer growth [1-4]. It has also been demonstrated that the presence of Sb on Ag, or O on Pt, can induce layer-by-layer homoepitaxial growth at conditions typical for island growth in the pure system [8,10]. Particularly in the case of homoepitaxy, these studies provide new opportunities for a better understanding of the mechanisms controlling growth kinetics.

In this Letter, we address surfactant-mediated layer-by-layer growth beginning at the fundamental level by analyzing the effects of the different atomic interactions in a given system. We restrict our discussion to metal-on-metal homoepitaxial growth, where we denote the adsorbed atoms by A and the surfactant atoms by S . We propose that, if the effective bond strengths satisfy the inequalities $V_{A-A} > V_{A-S} \gg V_{S-S}$, then a submonolayer of S atoms can act as a good surfactant in enhancing layered A -on- A growth. We will reach this conclusion by analyzing various local bonding geometries in searching for possible processes that are likely to enhance layered growth, then verifying the effects of these processes by direct simulations.

To facilitate the discussion we first establish some useful relationships from dimensional analysis. We consider a typical deposition process in the island growth regime, in which the diffusion length of the adatoms is insufficient for all atoms to reach steps. Islands therefore nucleate and grow, and additional atoms from the deposition beam may fall on top of these growing islands as well as onto the original substrate or other intermediate layer. As has been stressed previously [9,12,13], the decisive process controlling the smoothness of the growth front in homoepitaxy is interlayer mass transport: The morpholo-

gy will roughen if interlayer transport is insufficient to allow atoms to leave the tops of islands or clusters as fast as they are arriving. We introduce a determinant factor,

$$F \sim \frac{t_1}{t_0} \frac{N_p}{N_{\text{tot}}} \exp\left\{-\frac{V_e}{kT}\right\}, \quad (1)$$

where t_1 is the average time separation for two consecutive adatoms, A , landing on a given island, t_0 the residence time of an adatom spent at each site on the island, N_p the number of sites along the perimeter of the island, N_{tot} the total number of sites on the island, V_e the activation barrier for an adatom to step down from a site belonging to N_p , and kT the thermal energy. So far all sites are defined on top of the island. The first ratio in Eq. (1) gives the total number of hops made by the first atom landed on top of the island before being joined by a second atom; the second ratio gives the fraction of hop attempts to step down. To a good approximation, F measures the probability that an adatom A landing on an island will hop off to a lower layer before a second adatom lands on the same island. We assume that the value of V_{A-A} is large enough to make an $A-A$ dimer an effective nucleation center. Therefore, nucleation on top of an island before the layer defining the island is completed will be prohibited if F is large enough. Likewise, one expects to observe improved layer-by-layer growth behavior whenever the value of F is quantitatively enlarged.

If the growth starts on a two-dimensional substrate, $t_1 \approx 1/RA \sim 1/RL^2$, where R is the number of particles deposited per unit area per unit time and L is the dimension of the island. The inverse residence time can be written as $(t_0)^{-1} = v_0 \exp\{-V_u/kT\}$, where v_0 and V_u are, respectively, the attempt frequency and diffusion barrier of an A atom on top of the island. We can approximate $N_p/N_{\text{tot}} \sim 1/L$, and further identify [14] $L^{-3} \sim [R/\theta^2 a^2 v_0 \exp(-V_l/kT)]^{1/2}$, where V_l is the activation barrier for diffusion in the lower layer, a is the surface lattice constant, and θ is the coverage. Equation (1) can then be rewritten as

$$F \sim \left(\frac{v_0}{a^2 R}\right)^{1/2} \frac{1}{\theta} \exp\left\{-\frac{V_e + V_u - \frac{1}{2} V_l}{kT}\right\}. \quad (2)$$

It is clear from Eqs. (1) or (2) that there exist multiple possibilities to enhance the value of F . In a pure system, $V_u = V_l$, and $V_e + V_u - \frac{1}{2} V_l > 0$; therefore, the most efficient way to enhance the value of F is to increase the growth temperature. Because low-temperature layer-by-layer growth is often desired, the next choice is to reduce V_u or V_e [8,10]. Farther down on the list is to increase V_l [3]. One can also deliberately prepare the initial growth conditions to make the cluster dimension L smaller [9], therefore enhancing both factors $t_1/t_0 \sim 1/L^2$ and $N_p/N_{\text{tot}} \sim 1/L$. Finally, when the temperature is lowered to the regime of diffusion limited aggregationlike growth, the increase in the factor N_p/N_{tot} alone could overcome the decrease in the exponential factor (assuming none of the activation barriers is affected), leading to reentrant layer-by-layer growth [12].

Using these relationships, we discuss the influence of a surfactant satisfying $V_{A-A} > V_{A-S} \gg V_{S-S}$ on the modes of A -on- A growth. We first look at the morphology of the substrate before the deposition of A , but with a low coverage of the surfactant S on it. Because V_{S-S} is very small (in the sense that $V_{S-S} \leq kT$), the S atoms do not aggregate to form clusters. Instead, they wander freely on the substrate. Because $V_{A-A} > V_{A-S}$, and because diffusion barriers generally quantitatively scale with V , the corresponding activation barrier for such S -on- A diffusion is smaller than that for A -on- A diffusion.

Next we start depositing A atoms onto such a surface. We work in the regime where the surface temperature is not high (such that the pure A -on- A growth would be three dimensional), implying that both V_{A-A} and V_{A-S} are large compared with kT . Therefore, as soon as an A atom encounters an S atom, the A - S dimer would behave as an effective nucleation center for approaching S (if reaching the A side of the dimer) or A atoms. In the earliest stages of growth the number of clusters thus formed is proportional to the number of A atoms deposited. The density of nuclei far exceeds that formed by only the A atoms without the presence of the surfactant [6,9], making the effective island dimension L much smaller for a given dose. Therefore, even without any other modifications on the various hopping rates, the presence of the surfactant will at least enhance the layered growth of the first layer if judged by the number of incomplete layers [9].

Of course, a "smooth" layer of A - S mixture is rarely the desired structure. What is vital is for the surfactant atoms to live up to their name, that is, to float on the surface as growth proceeds. It is the inequality $V_{A-A} > V_{A-S}$ that makes such a requirement possible. Specifically, whenever an S atom is about to be buried in a layer by an A atom on top, incorporation of the A atom into the layer by exchanging with the S atom is highly probable. This process can be illustrated using Fig. 1. In Fig. 1(a), an A atom diffuses on an island containing an S atom. As the A atom attempts to hop to the right, it lifts the S atom out of the layer [Fig. 1(b)], then itself takes the position

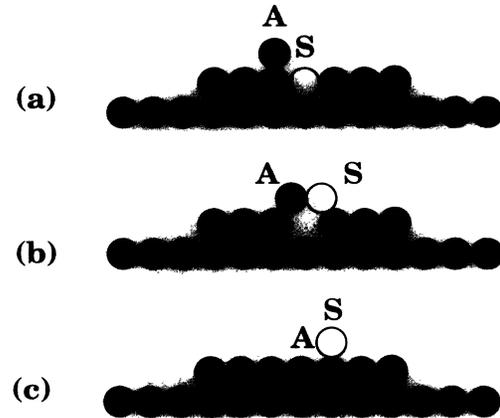


FIG. 1. An illustrative example showing how an adatom A lifts a surfactant atom S by an exchange process. The A atoms are represented by solid circles and the S atom by open circles. (a) Before the exchange; (b) the transition state; (c) after the exchange.

originally occupied by the S atom, leaving the S on top [Fig. 1(c)]. We recall that for metal-on-metal self-diffusion, exchange processes similar to the one shown here have been observed on both the fcc (110) and the (100) surfaces [15]. The *additional* energy favoring an A - S exchange in comparison to an A - A exchange is proportional to $n(V_{A-A} - V_{A-S})$, where $n \geq 2$ is the number of nearest-neighbor bonds that must be stretched or broken in reaching the transition state [Fig. 1(b)]. We stress that even if self-diffusion by such A - A exchange does not take place on a *pure* surface, when the surface is contaminated with S atoms within its top layer, the A - S exchange *may* become possible when an A atom diffusing on the surface migrates to the close vicinity of an S atom. It should be noted that if before the exchange the in-layer S atom has another in-layer S neighbor, the A - S exchange is kinetically even more favorable, because of the replacement of a strong V_{S-A} bond by a weak V_{S-S} bond. It is also important to note that, because the configuration shown in Fig. 1(c) is energetically much more stable if compared with Fig. 1(a), the reverse S - A exchange cannot take place, leaving the S atom floating on top of the island. For metal systems, we speculate that the A - S exchange mechanism as described here is the dominant process through which the surfactant atoms are lifted to avoid being buried. Similar exchange processes can also take place at a semiconductor interface [16]. For surfactant-mediated heteroepitaxial layer-by-layer growth in semiconductor systems, the exchange processes involved can be more complicated [3,7,17].

The incorporation of A into an A -dominant layer by A - S exchange effectively enhances the diffusion coefficient on *top* of the growing layer. That is, after the exchange, the initial A -on- A diffusion is replaced by S -on- A diffusion, whose motion is faster overall. Therefore, the S atom will reach the island edges more frequently. If the

fast-moving S atom reaches the S -terminated portion of the step edge, it may be harder for it to jump down by rollover than the A atom by exchange. But if it reaches the A -terminated portion, it should jump down faster than the A atom (if both by rollover). When the islands are small, effectively all S atoms will reach the steps and go down. If, on the other hand, the layer underneath the S atom is (nearly) completed so that the island is very large, the S atom will additionally act as a nucleation seed, initiating the growth of a new layer. The functioning of an S atom located at a kink site of the step edge will be discussed in the following paragraph.

Now we focus our attention on the step-down process. It has been observed experimentally that for an A atom stepping down at an A -terminated step, a push-out exchange process shown schematically in Fig. 2 can be favored over a direct "rollover" process [18]. The likelihood of an exchange process will be greatly enhanced if the step is S terminated. The *additional* energy favoring this A - S push-out exchange in comparison to an A - A push-out exchange is proportional to $2(V_{A-A} - V_{A-S})$ for the one-dimensional picture shown in Fig. 2. If the difference $V_{A-A} - V_{A-S}$ is large enough, the step-down barrier $V_{e,A-S}$ corresponding to an A - S push-out process can be considerably lower than the barrier $V_{e,A-A}$ corresponding to either an A - A push-out or a direct A -on- A rollover process. As shown in Eq. (2), a reduction in V_e will enhance layered growth. For completeness, we note that if an S atom terminating a step is pushed forward all the way to reach another island, then its next likely fate is again to be lifted by an A atom through the process shown in Fig. 1.

In order to assess the relative importance of the factors discussed above in influencing the growth morphology, we have carried out various model studies with and without a surfactant, using kinetic Monte Carlo simulations. The details of the simulation will be published elsewhere. Briefly, it is done in (1+1) dimensions, with a deposition rate of 1 ML/sec, where ML is monolayers. The hopping

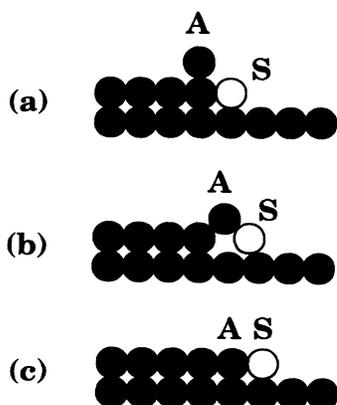


FIG. 2. A schematic picture showing how a surfactant atom attached to a step edge helps to lower the barrier for an adatom to step down.

rate of move i of either an A or an S atom is given by $R_i = R_0 \exp(-V_i/kT)$, where $R_0 = 2kT/h$. We choose the activation barrier for diffusion of an A atom on top of an A island to be 1.0 eV, and the corresponding rate to be the reference rate. All other rates are expressed in units of the reference rate. Such a choice of reference rate implies that an S atom moving on an A terrace will have a rate higher than 1. To account for this result we let an isolated S atom make m_S random hops whenever it is selected to move, where $m_S = \exp[(V_{A-A} - V_{A-S})/kT]$, with $V_{A-A} - V_{A-S} = 0.1$ eV. The barrier for either an A or an S atom to cross an A -terminated step edge is taken to be 1.2 eV. We assume that at the low growth temperatures of interest the strengths of both V_{A-A} and V_{A-S} are large enough, so that an A or S atom located at a kink site is stable if it has two strong bonds. In models where either the lifting of S to an upper layer (Fig. 1) or the push-out exchange (Fig. 2) is operative, the corresponding rate is set equal to the reference rate. We impose the restriction that neither type of exchange is allowed *unless* the process is favored both kinetically and thermodynamically by an energy difference $\delta V = n(V_{A-A} - V_{A-S})$, with $n \geq 2$. Finally, we neglect the value of V_{S-S} in computing configuration-dependent hopping barriers.

The simulation results for different models are shown in Fig. 3, where we plot the interface width $\xi(t)$ as a function of the mean film thickness $\langle h(t) \rangle$, with $\xi(t) = [\langle h^2(x,t) \rangle - \langle h(t) \rangle^2]^{1/2}$, $h(x,t)$ being the surface height at the point x . The surface temperature is 375 K.

Curve *a* is for pure A -on- A growth. The interface becomes increasingly rough as growth proceeds.

In curve *b*, the preadsorbed surfactant atoms have a coverage $\theta_S = 0.1$, but none of the processes shown in Figs. 1 or 2 are turned on. As expected [9], the surfactant enhances the layered growth of the first layer as signaled by the dip in $\xi(t)$ at $\theta_A + \theta_S = 1$, but after the first layer the growth becomes rough, because most of the surfactant atoms have been buried within the first layer. Similar results are obtained if the step crossing processes

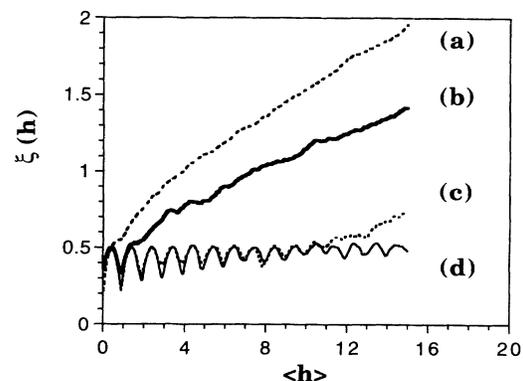


FIG. 3. The interface width as a function of the average film thickness, $\langle h \rangle \equiv \theta_A$, for different models. The surface temperature is 375 K for every case, and for *b-d* the surfactant coverage $\theta_S = 0.1$. For details, see text.

(Fig. 2) are switched on but not the lifting processes (Fig. 1).

In curve *c*, the lifting of *S* atoms by the *A-S* exchange (Fig. 1) is turned on, but step crossing (Fig. 2) is not allowed. It is clear that this joint mechanism (incorporation of *A* into a growing layer through exchange followed by faster motion of *S* on top of the layer) is quite effective in enhancing layer-by-layer growth. The interface width is increasing, but very slowly initially, with clear oscillations from layer to layer. For the deposition rate and potentials used here there are typically two incomplete layers at $\theta_A=5$, three at $\theta_A=10$, and four at $\theta_A=15$. Changing the parameters will obviously change the details of the curve, but the principle is illustrated.

Curve *d* results if both the lifting and the step crossing processes (Figs. 1 and 2) are allowed. Here nearly perfect layer-by-layer growth is achieved: When the total coverage $\theta_A+\theta_S$ is an integer, there are always only two incomplete layers, one close to complete and the other containing a few atoms. When $\theta_A+\theta_S$ is equal to a half integer, in many cases only the top layer is incomplete. We stress that in a real system several mechanisms can be operative, but the most important of all is the one shown in Fig. 1: Without this exchange process or a close analogy the *S* atoms cannot act as a good surfactant.

Finally we discuss the distribution of the surfactant atoms after depositing fifteen layers of *A* atoms. In model *d*, only about half of the preadsorbed 10% of *S* atoms remain on the top two layers and thus unburied, while the other half are scattered throughout the lower layers, resulting in an impurity concentration of $\leq 0.4\%$. Thus, while layering is enhanced, we have a metallurgically significant concentration of impurities in the film. We have also investigated the question of optimal surfactant coverage [9]. Clearly, if the surfactant coverage is too low, the processes enhancing layered growth as discussed here may not take place sufficiently frequently. On the other hand, if the surfactant coverage is too high, some of the *S* atoms will move up to the top of a growing layer and initiate the growth of a new layer well before the lower layer is filled mainly by the *A* atoms. Indeed, simulations at both $\theta_S=0.05$ and 0.4 result in interfaces rougher than that shown by curve *d* in Fig. 3. Furthermore, at $\theta_S=0.4$ more *S* atoms are buried in inner layers: The *S* atoms that move up to the top of a growing layer too early can bury the *S* atoms left underneath. In order to minimize the residual impurity concentration one needs to search for surfactants with sufficiently large bond strength differences ($V_{A-A}-V_{A-S}$): If this is true the exchange processes shown in Figs. 1 and 2 will take place more frequently, thus enhancing the floating ability of the surfactants.

To summarize, we have identified various competing processes that are likely to enhance layer-by-layer growth in the presence of a surfactant. Our results show that if the relative bond strengths satisfy the relations V_{A-A}

$> V_{A-S} \gg V_{S-S}$, then the *S* atoms can act as a good surfactant for layered *A-on-A* growth. Of all the competing processes, the one lifting the *S* atoms to the top layer of the growing interface by *A-S* exchange is most important. Our results suggest the existence of an optimal surfactant coverage and provide a criterion to minimize the concentration of surfactant atoms remaining as impurities in the film. In most cases of technological interest, this impurity concentration will likely be too high to make this a viable method of film growth. Nevertheless, the use of surfactants in film growth investigations will allow us to develop a better understanding of atomic-scale mechanisms in growth kinetics.

We would like to thank G. Comsa, T. Kuech, S. Liu, H. Metiu, C. Teichert, and M. B. Webb for helpful discussions and suggestions. This work was supported by NSF, Materials Research Group Grant No. DMR91-21074.

-
- [1] M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, *Phys. Rev. Lett.* **63**, 632 (1989).
 - [2] K. Fujita, S. Fukatsu, H. Yaguchi, T. Igarashi, Y. Shiraki, and R. Ito, *Jpn. J. Appl. Phys.* **29**, L1981 (1990).
 - [3] R. M. Tromp and M. C. Reuter, *Phys. Rev. Lett.* **68**, 954 (1992).
 - [4] H. J. Osten, J. Klatt, G. Lippert, E. Bugiel, and S. Higuichi, *J. Appl. Phys.* **74**, 2507 (1993).
 - [5] D. J. Eaglesham, F. C. Unterwald, and D. C. Jacobson, *Phys. Rev. Lett.* **70**, 966 (1993).
 - [6] B. Voigtlander and A. Ziner, *Surf. Sci.* **292**, L775 (1993).
 - [7] C. W. Snyder and B. G. Orr, *Phys. Rev. Lett.* **70**, 1030 (1993).
 - [8] H. A. van der Vegt, H. M. van Pinxteren, M. Lohmeier, E. Vlieg, and J. M. C. Thornton, *Phys. Rev. Lett.* **68**, 3335 (1992).
 - [9] G. Rosenfeld, R. Servaty, C. Teichert, B. Poelsema, and G. Comsa, *Phys. Rev. Lett.* **71**, 895 (1993).
 - [10] S. Esch, M. Hohage, T. Michely, and G. Comsa (to be published).
 - [11] *Encyclopaedia Britannica*, taken from citation 7 of Ref. [5].
 - [12] R. Kunkel, B. Poelsema, L. K. Verheij, and G. Comsa, *Phys. Rev. Lett.* **65**, 733 (1990).
 - [13] Z. Y. Zhang, J. Detch, and H. Metiu, *Phys. Rev. B* **48**, 4972 (1993).
 - [14] Y.-W. Mo, J. Kleiner, M. B. Webb, and M. G. Lagally, *Surf. Sci.* **268**, 275 (1992).
 - [15] See the recent review by P. J. Feibelman, *Comments Condens. Matter Phys.* **16**, 191 (1993), and references therein.
 - [16] D. J. Jesson, S. J. Pennycook, and J.-M. Baribeau, *Phys. Rev. Lett.* **66**, 750 (1991).
 - [17] E. Kaxiras, *Europhys. Lett.* **21**, 685 (1993).
 - [18] S. C. Wang and G. Ehrlich, *Phys. Rev. Lett.* **67**, 2509 (1991).

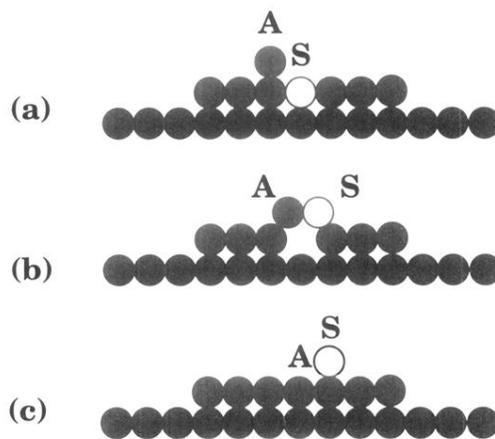


FIG. 1. An illustrative example showing how an adatom A lifts a surfactant atom S by an exchange process. The A atoms are represented by solid circles and the S atom by open circles. (a) Before the exchange; (b) the transition state; (c) after the exchange.

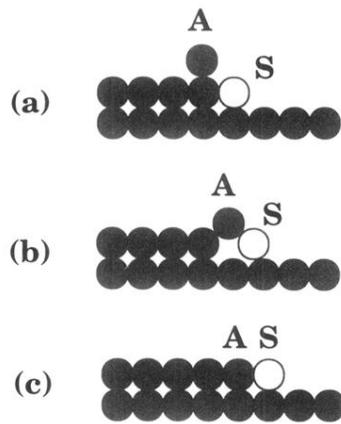


FIG. 2. A schematic picture showing how a surfactant atom attached to a step edge helps to lower the barrier for an adatom to step down.