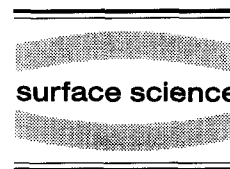




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Submonolayer island growth with adatom exchange

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Abstract

Submonolayer epitaxy is studied with two simple theoretical models where adatom exchange with a surface atom yields a stable nucleus for island growth. The results are relevant to systems where surface layer inclusions are formed by alloying and where buried islands are formed in the presence of surfactants. Rate equations and Monte Carlo simulations are used to study the evolution of the island size distributions. The rate equations reproduce all of the qualitative features found in both the simulations and in recent experiments when the coverage-dependent rate of adatom capture by islands is calculated self-consistently.

Keywords: Growth; Models of non-equilibrium phenomena

The traditional view of epitaxial growth in the nucleation regime supposes that the process is initiated by binary collisions between deposited adatoms that diffuse on the surface. The resulting dimer island "nucleus" may or may not be stable against dissociation before the arrival and attachment of further adatoms. So long as the adatom concentration on the surface exceeds its equilibrium value, an island population develops that exhibits a maximum in the vicinity of the average island size. The correctness of this scenario in the pre-coalescence regime, originally made quantitative by the use of rate equation theory [1], now has been established unequivocally with atomistic kinetic Monte Carlo simulations [2] and scanning tunnelling microscopy (STM) [3].

Recently however, it has become clear that another scenario is possible: a stable island nucleus

that consists of a *single* atom can be created by the spontaneous *exchange* of a diffusing adatom with an atom in the surface layer below. A new form of island growth occurs if other diffusing atoms experience an enhanced probability to exchange when they encounter previously exchanged atoms. For metals, this type of incipient surface alloying has been observed for Fe/Cu(001) [4], Au/Ni(110) [5], Fe/Au(001) [6], and predicted for Sb/Al(111) [7]. For semiconductors, the same type of exchange mechanism is envisaged between surface species and impurity or surfactant species that float to the surface of the growing crystal. Examples include heteroepitaxial (Sb,As)/Ge(001)/Si(001) [8] and Te/InAs(001)/GaAs(001) [9] and homoepitaxial In/GaAs(111)B [10].

For the Fe/Cu(001) system, Chambliss and Johnson (CJ) [11] have presented STM data for the number density of surface "inclusions" that contain *s* Fe atoms. In the data of CJ, the measured population

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density N_s exhibits no peak in the vicinity of the average inclusion size, quite unlike the results found for the conventional binary collision scenario. Instead, the CJ data more nearly resemble a non-increasing function of s . To explain these results, CJ set up the Smoluchowski-type rate equations

$$\frac{dn}{dt} = F - Dn \sum_{s \geq 0} \sigma_s N_s, \quad (1)$$

$$\frac{dN_s}{dt} = Dn(\sigma_{s-1}N_{s-1} - \sigma_s N_s), \quad (s > 0). \quad (2)$$

The symbols here are as follows: n is the density of adatoms; F is the deposition rate; D is the adatom diffusion rate; σ_0 is the probability per diffusion step that an adatom exchanges with a substrate atom; N_0 is the density of substrate sites available for exchange; and σ_s is a capture number [1,2] that reflects the effect of diffusion on the rate at which adatoms encounter and irreversibly join an inclusion composed of s atoms. These equations presume that mobile adatoms never encounter one another and take no account of the fate of the exchanged substrate atoms. Similar equations were envisaged (but not explicitly written down) by Venables and Price [12] in their discussion of nucleation in the presence of "strong adatom traps".

CJ found an exact solution to their rate equations for the special case $\sigma_s = 1$ ($s > 0$) and presented numerical solutions for $\sigma_s \propto s^p$ ($0 < p < 1/2$). Semi-quantitative agreement with the STM data below about 10% coverage was found for N_s and the total inclusion density $N = \sum_{s>0} N_s$ with $\sigma_0 \sim 10^{-3}$ although the scatter in the data precluded a detailed comparison.

The purpose of the present Letter is to study the question of island size distributions in the presence of adatom exchange using two models that complement and extend the discussion in Ref. [11]. We begin with a slightly more complete discussion of the behavior of the adatom and total island density in the case studied by CJ and then solve the rate equations using a more detailed treatment of the capture numbers. Our calculation makes use of the fact [1,2] that each capture number σ_s varies with total coverage $\theta = Ft$ in a manner that can be calculated self-consistently within a simple mean field theory. The results exhibit a distinct new feature that may be present in the existing data. Second, we present results from a simple kinetic Monte Carlo simulation that largely confirm the ana-

lytical results of the mean field theory.

To begin, we sum over s in Eq. (2) to obtain the contracted equations

$$\frac{dn}{dt} = F - \sigma_0 D N_0 n - \bar{\sigma} D N n, \quad (3)$$

$$\frac{dN}{dt} = \sigma_0 D N_0 n, \quad (4)$$

where $\bar{\sigma} = N^{-1} \sum_{s>0} \sigma_s N_s$ is the average capture number. In the experimentally interesting limit $N \gg n$, the total coverage θ can be identified with the variable $\theta = \theta - n$ and CJ found that

$$N_{\text{CJ}}(\theta) = \frac{\sigma_0}{\bar{\sigma}} [\sqrt{1 + 2\bar{\sigma}\theta/\sigma_0} - 1], \quad (5)$$

when $\bar{\sigma}$ is not a function of θ .

It is a simple and useful generalization to lift the restriction $N \gg n$ used to obtain Eq. (5) so that easy comparison can be made with rate equation studies of the conventional binary collision scenario [2,13]. As in Ref. [11], we maintain $\theta \ll 1$ so that $N_0 = 1 - \theta$ can be regarded as constant and ensure that $F/D \ll \sigma_0^2$ so that binary collisions between adatoms can be neglected throughout [14]. One then easily checks that the third term on the RHS of Eq. (3) can be neglected at the shortest times so that

$$\begin{aligned} n &= \theta, & \theta &\leq \theta^*, \\ N &= \frac{D}{2F} \sigma_0 N_0 \theta^2, & \theta &\leq \theta^*, \end{aligned} \quad (6)$$

where θ^* is the coverage when the gain of adatoms by deposition is first balanced by the loss due to exchange with the substrate. This happens to occur at the point when the adatom and total islands densities become almost equal, i.e.,

$$N^* \simeq n^* = \theta^* = \frac{F}{D\sigma_0 N_0}. \quad (7)$$

Thereafter, it is sufficient to set the LHS of Eq. (3) equal to zero so that

$$n = \frac{F/D}{\sigma_0 N_0 + \bar{\sigma} N}, \quad \theta \geq \theta^*. \quad (8)$$

Substituting Eq. (8) into Eq. (4) and integrating yields

$$N(\theta) = N^* + N_{\text{CJ}}(\theta - \theta^*), \quad \theta \geq \theta^*, \quad (9)$$

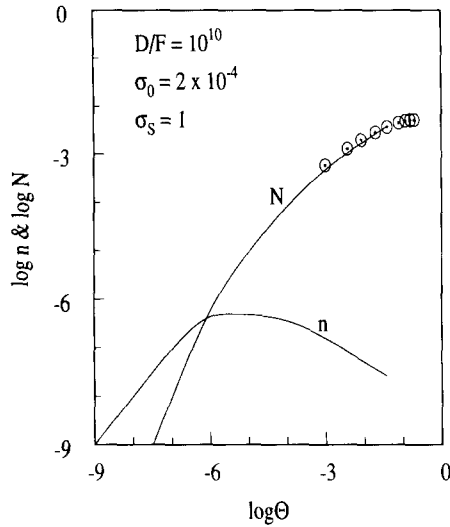


Fig. 1. Coverage dependence of the adatom density $n(\theta)$ and total island density $N(\theta)$ as computed from Eqs. (1) and (2) with all $\sigma_s = 1$. The circles are $N(\theta)$ obtained from a Monte Carlo simulation. See text for discussion.

which can be substituted back into Eq. (8) to obtain $n(\theta \geq \theta^*)$. Direct numerical integration of the original rate equations (with all $\sigma_s = 1$) confirms these simple considerations. For example, the veracity of the power law predictions are evident from the (nearly) straight lines in the log-log plots of Fig. 1. Note also the quantitative agreement with (7) and the fact that the plateau in $n(\theta)$ at the value n^* occupies the interval $\theta^* \leq \theta \leq \sigma_0$.

We turn next to an improved treatment of the capture numbers that takes account of the effect of exchange and aggregation on the adatom diffusion problem. To do so, we generalize to the present case the analysis by Bales and Chrzan [2] of the binary collision scenario. The capture numbers σ_s are calculated from

$$\sigma_s = \frac{2\pi R_s}{n} \left. \frac{\partial n}{\partial r} \right|_{r=R_s} = 2\pi \frac{R_s}{\xi} \frac{K_1(R_s/\xi)}{K_0(R_s/\xi)}, \quad (10)$$

where the island radii $R_s = \sqrt{s/\pi}$ and $K_1(x)$ and $K_0(x)$ are modified Bessel functions. The latter arise from a quasi-static solution to a diffusion-reaction equation for the spatial variation of the adatom concentration $n(r)$ in the vicinity of a circular island of radius R_s :

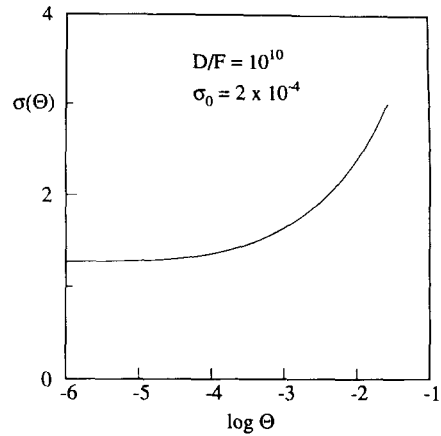


Fig. 2. Coverage dependence of the self-consistent average capture number.

$$\frac{\partial n}{\partial t} = D \nabla^2 n(r) + F - \frac{D}{\xi^2} n(r). \quad (11)$$

The quantity ξ , the mean distance an adatom diffuses before irreversible capture by an island or exchange with the substrate, is computed self-consistently at each time step from Eq. (10) and

$$\frac{1}{\xi^2} = \sum_{s=0} \sigma_s N_s. \quad (12)$$

The adatom density n that enters all of the above equations is the spatial average of the quantity $n(r)$ calculated from Eq. (11). Further details may be found in Ref. [2].

When calculated as sketched above, the absolute values of the individual capture numbers are found to be nearly independent of both the exchange probability σ_0 and the deposition conditions so long as $D/F > 10^9$. In particular, they obey $\sigma_{s+1} > \sigma_s$ and increase monotonically with coverage. The behavior of individual capture numbers σ_s is well represented by the behavior of the average $\bar{\sigma}$, shown in Fig. 2. This semi-logarithmic plot makes clear that no simple power law parameterization can provide an adequate description of the coverage dependence. Given this, the variation of n and N when $\theta \geq \theta^*$ cannot be identical to that shown in Fig. 1, which assumed a constant value for all σ_s . But the differences in the variation of n and N with θ when self-consistent σ_s 's are used turn out to be small, so we do not elaborate further here. Instead, we turn to the island size distributions.

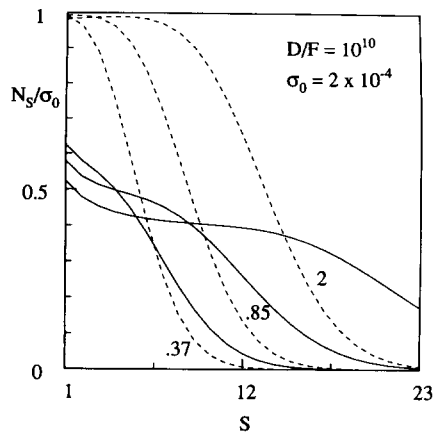


Fig. 3. Normalized island size distributions as computed with all $\sigma_s = 1$ (dashed curves) and with capture numbers computed self-consistently (solid curves) at 0.37%, 0.85% and 2.0% coverage.

Fig. 3 illustrates $N_s(\Theta)$ at three coverages computed numerically from Eq. (1) and Eq. (2) both with all $\sigma_s = 1$ and with the capture numbers computed self-consistently. We note in passing that the parameters used and coverages shown in this figure represent a compromise between typical experimental values and the prickly convergence properties of the rate equations. In accord with the results of Ref. [11], the dashed curves ($\sigma_s = 1$) exhibit a saturation of the population densities to the value σ_0 at small s . This effect is not present in our self-consistent results (solid curves) because, as noted above, the s -dependence of our capture numbers (at fixed coverage) reflect a relatively greater capture efficiency for large islands. CJ found similar behavior for their choice $\sigma_s \propto s^p$. But the details of their N_s curves differ from ours. In particular, our calculations yield a distinct "knee" in the distribution function that we believe is present in the STM data for Fe/Cu(001) [11]. We do not attempt a quantitative comparison owing to the large statistical fluctuations evident in the experimental data sets.

The systematics of the knee are better appreciated when the island size distributions are replotted in a scaled form first used in connection with the binary collision epitaxy problem by Bartelt and Evans [15]. To do so, one computes the average island size s_{av} at each coverage and plots $s_{av}^2 N_s / \Theta$ versus s/s_{av} . As seen in Fig. 4, this scaling *ansatz* collapses curves of N_s at different coverages onto (nearly) a single

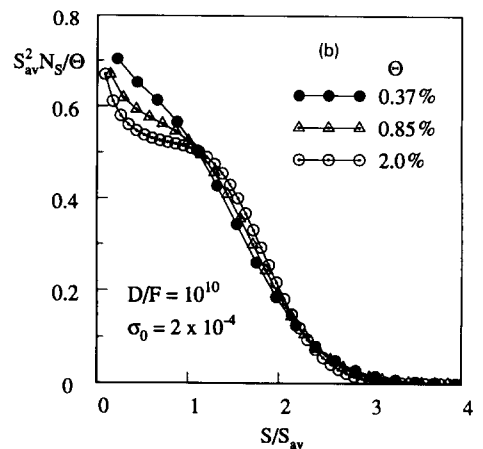
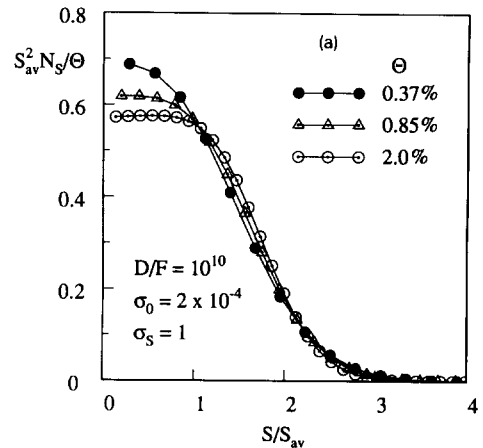


Fig. 4. Same results as Fig. 3 plotted in scaled form. (a) all $\sigma_s = 1$; (b) σ_s computed self-consistently.

curve. Excellent collapse is found for both the non-self-consistent results and the self-consistent results when $s > s_{av}$. But the two deviate from one another and scaling appears to fail at these coverages when $s < s_{av}$. For the self-consistent calculations, the crossover at $s = s_{av}$ is precisely the inflection point where the knee is most pronounced. The reason for this behavior, in terms of the microscopic behavior of island growth, is unclear at present.

Of course, the rate equations represent at best a mean field solution to the real problem. To test these results, Monte Carlo simulations of island growth in the deposition-and-exchange scenario were performed as follows: (i) an atom is deposited at random onto a site of an $L \times L$ square lattice; (ii) the atom is immobi-

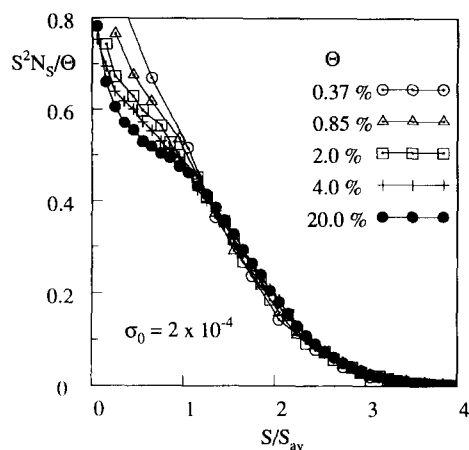


Fig. 5. Scaled island size distribution obtained from a Monte Carlo simulation. The data collapse onto a single curve for $\theta \geq 5\%$. The data for $\theta = 4\%$ are barely discernible from the collapsed curve. The data for lower coverages show significant and systematic deviations from the collapsed curve (see text for details).

lized at that site (“exchanges”) with a probability σ_0 (chosen equal to the value used in the rate equations); otherwise, it is moved one lattice constant to a nearest neighbor site chosen at random; (iii) the previous step is repeated until exchange occurs or until the wandering atom becomes a nearest neighbor to a site where exchange has occurred already, whereupon it exchanges with unit probability [16]. The entire process is repeated one atom at a time until the desired coverage is reached. Clearly, the foregoing is meant to represent a situation when the ratio D/F is very large. In practice, the system size provides the bound $D/F > L^2$.

The simulations were performed with periodic boundary conditions on square lattices of size $L = 1024$ for coverages $\theta \leq 2\%$ and $L = 512$ for larger coverages. The larger lattice size was necessary to obtain good statistics for very low coverages. All results represent an average over at least 400 samples at each value of the coverage. Additional realizations at selected coverages made no discernible difference. Over the range of coverages for which we can collect good statistics, the total island density $N(\theta)$ obtained from the simulations accords very well with the contracted rate equation treatment described earlier (Fig. 1). More interesting perhaps is the scaled island size distribution (Fig. 5). Data collapse is found for all coverages between about 5% and 20% [17], whereas

systematic deviations from scaling are found at low coverage when $s < s_{av}$. Both results are in excellent agreement with our rate equation results. Significantly, there is *no* evidence that scaling fails at very low coverage for the conventional binary collision problem [2].

Direct comparison of Fig. 5 with Fig. 4 shows that the knee found in our rate equation treatment is quite real. Even the systematics of the deviations from scaling behavior at the smallest coverages are well reproduced. We conclude that Eqs. (1) and (2) used in conjunction with *self-consistently* determined capture numbers are quite sufficient to account for all the essential features of the island size distribution for the adatom exchange epitaxial growth problem.

Acknowledgements

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