Mean-Field Theory of Quantum Dot Formation

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The formation of undislocated three-dimensional (3D) islands during semiconductor heteroepitaxy is studied using self-consistent rate equations. Lattice misfit strain is presumed to influence the rate at which atoms detach from two-dimensional (2D) islands and the rate at which 2D islands transform to 3D islands. The calculated dependence of the 3D island densities on growth rate and coverage compares favorably with experimental results for InP grown on GaP-stabilized GaAs(001) by metal-organic vapor phase epitaxy. [S0031-9007(97)03763-0]

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Dislocation-free (coherent), three-dimensional (3D) islands that form spontaneously atop one or a few complete wetting layers during heteroepitaxial growth of lattice-mismatched semiconductors [1] have generated intense interest in recent years. The optical spectra of such islands exhibit quantum confinement effects [2], and their narrow size dispersion and spatial self-organization [3] suggest a number of potential device applications. This so-called Stranski-Krastanov (SK) growth mode has been demonstrated for a variety of material systems [4,5]. But before SK growth can become a robust method of producing quantum dots, it is desirable to have a simple and predictive model of the growth kinetics.

Priester and Lannoo [6] performed energetic calculations to determine at what size a collection of uniformly sized and spaced two-dimensional (2D) strained islands would transform to 3D pyramidal islands of the same volume. The transformation of all islands was taken to be abrupt with a 3D size distribution characteristic of an *equilibrium* ensemble of the precursor 2D islands. However, it is well known that epitaxial island-size distributions bear no resemblance to equilibrium distributions [7].

A more recent analysis [8] also employed the notion that a 2D island transforms to a 3D island when it exceeds a fixed critical size. To determine how many 3D islands appear as deposition proceeds, they make use of a parametrized scaling form for the time evolution of a 2D island-size distribution appropriate to *homoepitaxy*. This approach indeed reproduces the sudden onset of 3D nucleation seen in many SK systems [9,10], but the 2D distribution parameters were chosen to fit the observed 3D density at one particular temperature and growth rate, and no rationale was provided to make the theory predictable for other growth conditions [11].

In this paper, we present a true kinetic model that yields the time dependence of the 3D island density and describes how this density varies with external growth conditions. We compare our results to extensive measurements of the density of 3D islands formed during the deposition of InP on a GaP-stabilized GaAs(001) surface by metal-organic vapor phase epitaxy (MOVPE) [12] over a range of temperatures and growth rates.

Our model generalizes a well-known rate equation theory of epitaxial growth [13]. The primary dynamical variables are the densities of (Group III) adatoms n_1 and of 2D and 3D islands, denoted by n and $\tilde{n}$, respectively [14]. Spatial information is omitted in this mean-field theory, but with a suitable description of adatom capture, quantitative agreement with Monte Carlo simulations for adatom and (2D) island densities can be achieved [15,16]. We consider four types of processes that cause n_1, n and $\tilde{n}$ to change.

Deposition.—Atoms arrive at and adsorb to the growing surface at a rate F determined by the growth rate. The wetting layers are presumed to have already formed.

Diffusion.—Adatoms are the only mobile surface species. They migrate with diffusion constant $D = (2k_BT/h)\exp(-E_S/k_BT)$, where k_B is Boltzmann's constant, T is the temperature, h is Planck's constant, and E_S is an energy barrier to hopping between surface sites. The spacing between surface sites is our unit of length.

Attachment and detachment.—As adatoms diffuse over the surface, they collide and form immobile islands. We assume that 2D islands composed of not more than i^* atoms are thermodynamically *unstable* and quickly break up into adatoms. Larger 2D islands are stable and grow by capturing adatoms, although strain-induced detachment of atoms from their perimeter becomes increasingly important as their size increases (see below). We use the

Walton relation [17] for the density of critical nuclei

$$n_{i^*} \approx \exp(E_{i^*}/k_BT) n_1^{i^*}, \qquad (1)$$

where E_{i^*} is the binding energy of a critical island.

The contracted rate theory that we used focuses on an "average" 2D island composed of s atoms with radius r and an average 3D island of $\tilde{s}$ atoms with radius $\tilde{r}$ [18]. Attachment to islands occurs at a rate proportional to the adatom density. For 2D islands this rate is $D\sigma n_1$, which defines the "capture number" for 2D islands σ. Capture numbers for critical islands σ_{i^*} and 3D islands $\tilde{\sigma}$ are defined similarly. A constant energy barrier E_a is presumed to augment the surface diffusion barrier E_S for adatoms attaching to both 2D and 3D islands. This is important in MOVPE, where step decoration by reaction products can inhibit attachment [19].

Atoms detach at a rate w from 2D islands significantly larger than the critical island at a rate

$$w = 2\pi r D \exp[-E_d(s)/k_BT]. \qquad (2)$$

As an island grows there is a strain- and size-dependent reduction in the barrier $E_d(s)$ for atomic detachment from the island perimeter [20]

$$E_d(s) = E_d(\infty) + E_0 \frac{\ln r}{r}. \qquad (3)$$

We take $E_d(\infty) = 0$ since the barrier is expected to become small for large islands. For 3D islands, constituent atoms are considered never to detach, but instead migrate to other sites on the same island to maximize strain relief.

For use in the rate equations, we calculate the capture numbers and perimeter atom escape rates from 2D islands using a self-consistent scheme [13,15] generalized to include detachment processes and attachment barriers [16]. The coverage-dependent capture number is

$$\sigma = \frac{2\pi r K_1}{\beta^{-1} K_1 + \xi K_0}, \qquad (4)$$

where $\beta^{-1} = \exp(E_a/k_BT) - 1$, $K_0 = K_0(r/\xi)$, and $K_1 = K_1(r/\xi)$ are zeroth- and first-order modified Bessel functions, and ξ is determined self-consistently by

$$\xi^{-2} = (i^* + 1)\sigma_{i^*} n_{i^*} + \sigma n + \tilde{\sigma}\tilde{n}. \qquad (5)$$

For critical islands and 3D islands, the capture numbers σ_{i^*} and $\tilde{\sigma}$ can be calculated using the same formulas with the appropriate radii [18]. The escape rate from 2D islands is [16]

$$\frac{1}{\tau} = \frac{w\sigma}{2\pi r} \exp(E_a/k_BT), \qquad (6)$$

where w is the detachment rate given in (2). Note that one must distinguish the escape rate $1/\tau$ from the detachment rate w because detaching atoms may be recaptured immediately by their parent islands [16].

2D-3D transition.—As a 2D island grows, it becomes increasingly likely that a second layer will nucleate on top of it. To estimate the rate for this process, consider a 2D island where adatoms detach from perimeter sites and jump onto the top surface at a rate proportional to the detachment rate w. If the island is small compared to the diffusion length, the density of adatoms ρ on top of the island is uniform, and the rate at which adatoms fall off the island edge is $2\pi r D \rho \exp(-E_e/k_BT)$, where E_e is an extra barrier for atoms to cross step edges. In steady state, $\rho \approx \exp\{[E_e - E_d(s)]/k_BT\}$, and the nucleation rate for the second layer is $\pi r^2 D \rho^{i^*+1} \exp(E_{i^*}/k_BT)$, so

$$\gamma = \pi r^2 D \exp\{E_{i^*} + [E_e - E_d(s)](i^* + 1)/k_BT\}. \qquad (7)$$

After the second layer nucleates, atoms detaching from the island base and any adatoms that attach to the island find their way to second and yet higher layers, where the strain is relieved, and the island soon becomes three dimensional. Thus, we take γ as the rate at which 2D islands transform to 3D islands.

This 2D-3D transition mechanism is different from that based on a critical 2D island size [6,8], although the rate γ is very strongly size dependent due to the barrier $E_d(s)$. In fact, we find that islands smaller than the limiting size in Refs. [6] and [8] are likely to transform. However, because the strain is relaxed in 3D islands, reducing the rate of atom detachment, they grow rapidly, so small 3D islands will not be observed.

Given the foregoing, the rate equations for the densities of adatoms, 2D and 3D islands are

$$\begin{aligned} \dot{n}_1 &= F - D[(i^* + 1)\sigma_{i^*} n_{i^*} + \sigma n + \tilde{\sigma}\tilde{n}] n_1 + n/\tau, \\ \dot{n} &= D\sigma_{i^*} n_{i^*} n_1 - \gamma n, \\ \dot{\tilde{n}} &= \gamma n, \end{aligned} \qquad (8)$$

which are supplemented by two equations for the average sizes of 2D and 3D islands,

$$(\dot{ns}) = D[(i^* + 1)\sigma_{i^*} n_{i^*} + \sigma n] n_1 - \gamma s n - n/\tau, \qquad (9)$$

$$(\dot{\tilde{n}\tilde{s}}) = D\tilde{\sigma}\tilde{n} n_1 + \gamma s n. \qquad (10)$$

The initial conditions for the island densities are $n_1 = n = \tilde{n} = 0$. The zero for the time t is taken when the final completely full wetting layer stops growing. These equations are *generic* to any mean-field theory of quantum dot formation in which 2D islands transform into 3D islands. However, the use of the Walton relation, necessary to close the equations, and our choices for the kinetic coefficients, which are estimates based on assumed mechanisms, are not generic and may be modified to suit other requirements.

Our model has six parameters: E_S, E_{i^*}, E_0, E_a, E_e, and i^*. Their values were determined by fitting the calculated 3D island density, as a function of growth rate and temperature, to experimental data at one coverage obtained from the growth of InP on GaP-stabilized GaAs(001) using MOVPE. Experiments [12] were carried out in a low pressure (100 mbar), radio frequency (RF)-heated MOVPE reactor. Trimethylgallium, trimethylindium, PH_3, AsH_3 and GaAs(001) substrates were used in H_2 as a carrier gas. After growing a GaAs buffer layer and a 2 ML thick GaP layer, 3.5 ML InP was deposited. Growth rates investigated were 0.17 (only for 883 K), 0.5, 0.7, 1.167, 1.75, and 3.5 ML/s for temperatures of 853, 883, and 913 K. The samples were then annealed for 12 s under PH_3 at the deposition temperature before cooling down. Atomic force microscopy (AFM) images were recorded in contact mode with a TopoMetrix TMX 2010 Discoverer instrument, and then island densities were calculated by counting islands on two $5 \times 5\ \mu m^2$ scans for each sample.

The data collected for a coverage of 3.5 ML and the results of the rate theory are shown in Fig. 1. Typical errors for the measured 3D density are $\pm 5.0 \times 10^8\ cm^{-2}$, so the comparison between the experimental data and the model is acceptable. For low growth rates the 3D density is an increasing function of the growth rate and a decreasing function of temperature. In this limit the density of 3D islands is controlled by the density of 2D islands that nucleate on the wetting layer. This increases as the growth rate increases or the temperature decreases. Surprisingly, the theory predicts that the 3D density actually *decreases* for large enough growth rates at a fixed temperature. This can be understood from the observation that, although the number of 2D islands continues to increase with increasing growth rate, the average size of these islands eventually falls below the value at which the 2D-3D conversion rate γ is appreciable. Such a decrease at large growth rates has, in fact, already been observed (but not explained) for MOVPE growth of InP/GaAs(001) [21].

Figure 2 compares the measured evolution of the 3D island density as deposition proceeds with the results of our model using the same parameters used in Fig. 1. The agreement is quite acceptable, including the position of the steep onset. The "dog-leg" shape of this curve is a result of the time variation of the 2D island size. Just after the completion of the wetting layer, only small 2D islands have nucleated, so the conversion rate γ is small. By approximately 2.3 ML, the islands reach a size at which conversion may begin, and the 3D density starts to increase, but with neither a simple exponential nor a simple power law [9] time dependence. As soon as 3D islands nucleate, they act as traps not only for adatoms that are deposited but also for atoms detaching from 2D islands. Thus, the 2D island size suddenly decreases and γ becomes small again, so that 3D nucleation abruptly stops.

Our rate theory is designed to describe 3D island evolution in just enough detail to reliably predict average quantities. Five "atomistic" energy parameters have been defined, but it should be clear that they function here as *effective* quantities in a severely contracted model that makes no attempt to describe the extremely complex MOVPE process in microscopic detail. All of these parameters are expected to be dependent upon strain and the choice of materials. The quantities E_S [22] and E_0 [23] can be expressed in terms of the strain and material-dependent quantities or calculated explicitly, but for E_e a specific atomistic mechanism for interlayer hopping must be assumed. Moreover, the fit in Fig. 1 is sensitive only to the *sum* of the parameters E_S and E_{i^*} (with small variations in the other parameters), a situation that is familiar from the conventional 2D nucleation

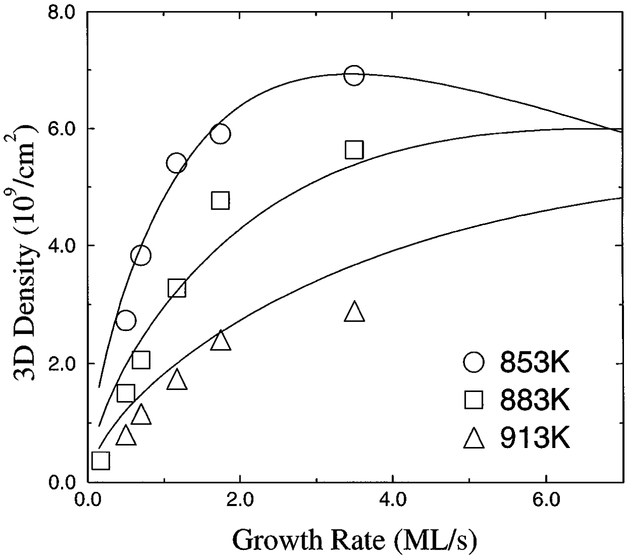

FIG. 1. Measured (symbols) and calculated (solid line) 3D island densities after 3.5 ML deposition. The optimized model parameters are $i^* = 6$, $E_S = 1.04$ eV, $E_{i^*} = 0.87$ eV, $E_0 = 3.28$ eV, $E_e = 0.17$ eV, and $E_a = 0.10$ eV.

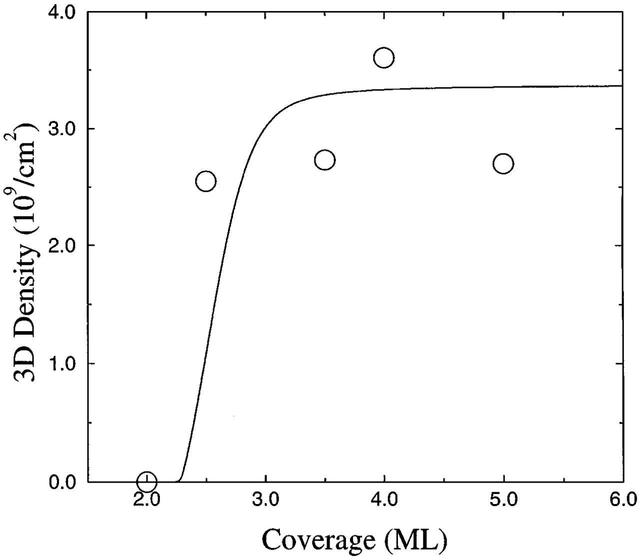

FIG. 2. Measured (symbols) and calculated (solid line) 3D island density versus coverage at a growth temperature of 853 K and a growth rate of 0.5 ML/s.

problem for submonolayer homepitaxy [13]. Acceptable fits can also be achieved for all values of $i^* > 2$. This reflects the rather weak dependence of our model on this parameter, which arises perhaps from the known effect of an attachment barrier on the i^* dependence of island densities for the conventional problem [19]. Thus, of the six free parameters in our model, accurate determination of only four is necessary.

Completed monolayers are inert in the classical picture of SK growth, but there is evidence in *some* SK systems that the total material contained in 3D islands exceeds that deposited after the wetting layer forms [9,24,25]. This implies that atoms that detach from the wetting layer are readily accommodated by the 3D islands. We have performed additional calculations using a scheme that includes a dynamic wetting layer of this sort [14] and found no significant change in the calculated density of 3D islands, except possibly at the highest temperature and lowest growth rate. The major difference is for the predicted volume of 3D islands, for which we do not have reliable data in the present case. It is also conceivable that such detachment processes depend on the growth technique used, with the presence of reaction products at step edges during MOVPE being an inhibiting factor.

The 3D island size distribution was not calculated explicitly here. But any nonzero value for the barrier E_a to adatom incorporation reduces the net flux of adatoms to every island (compared to the $E_a = 0$ case) and thus acts similarly to detachment processes acting alone. The latter situation has been studied with Monte Carlo simulations of homoepitaxy, where increasing rates of detachment lead to a progressive narrowing of the island size distribution [26]. In a more sophisticated version of the present theory [14], a strain-induced E_a increases as 3D islands grow in size. At late times, one thus expects a very narrow distribution around a self-limiting size. In the model presented here, the signature for this effect is a saturation of the average 3D island size $\tilde{s}$.

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