

Selective nucleation and controlled growth: quantum dots on metal, insulator and semiconductor surfaces

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Abstract

Nucleation and growth models are well developed for nucleation on homogeneous substrates, and can typically be described in terms of three energy parameters. Nucleation on substrates containing point defect traps has been investigated, at the cost of introducing more energy parameters. This paper outlines the quantitative description of such growth models, using rate and rate-diffusion equations, in terms of energies for individual surface processes, with examples taken from metal-metal, metal-insulator and semiconductor growth. The challenge to modelling is to describe the large range of length and time scales in thin film fabrication and degradation, without relying on too many (unknown) material parameters, which often occur in combination. Separating them into elementary processes often proves to be a challenge. One typically requires selective nucleation using patterned substrates, in combination with controlled, self-organized, growth for reliable nanotechnology. Reconstructed semiconductor surfaces offer both a further challenge to modelling and an opportunity for future technology; these paradoxes are discussed as space permits.

Key index words: Nucleation and growth; rate equations; rate-diffusion equations; metal growth; patterned substrates; semiconductor growth.

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1. Introduction

Nucleation and growth on surfaces has been intensively studied over the last thirty years. In the specific case of deposition from the vapour, it is well known that individual atomic events can strongly influence and even dominate the final micro- or nano-structure of epitaxial thin films (Venables 1994, 2000). Scanning tunneling microscopy (STM) (Brune 1998, Bennett & Von Känel 1999) and field ion microscopy (FIM) (Ehrlich 1991, 1994, Kellogg 1994, Tsong 1990) experiments are able to follow such individual events. Such experiments, which exploit the surface sensitivity and ultra-high resolution of the STM and FIM, have mostly been carried out on clean, low index metal surfaces at low temperatures, and have emphasized the extreme kinetic limit, where the main process is surface diffusion by individual adatoms, and pairs of adatoms already are stable clusters. Analysis of such experiments has led to accurate values of the adatom diffusion coefficient D_1 and diffusion energy (E_d and E_m are used in the literature), which have been tabulated in several cases in the above references.

On the other hand, experiments at higher temperature have required more parameters for their interpretation, but the order of events depends on the system studied. For metals deposited onto insulators such as alkali halides, the adatom adsorption energy E_a is typically the first additional parameter needed, as the metal adatom is rather weakly bonded to the substrate. In this case re-evaporation can take place at moderate temperatures, and the mean free path for adatoms is determined by $(E_a - E_d)$. For other systems, such as metal or semiconductor growth, $(E_a - E_d)$ is relatively high, so that the first process to intervene may be the breakup of small clusters, which can be parametrized by a lateral binding energy E_b between adatoms. Experiments on all these systems have been carried out by the full range of surface analytic and microscope techniques, including, where practical, *in-situ* observations of the nucleation and growth dynamics at the growth temperature. However, many growth methods, for example the widely used chemical vapour deposition (CVD), are much too complex for this approach to work; we have to rely almost entirely on *ex-situ* observations taken after growth at elevated temperature and subsequent cooling, typically to room temperature.

There are three main types of model which are used to connect these experiments to atomic-level parameters. The first, rate equations (RE) and rate-diffusion equations, has a long history in chemical kinetics; this largely deterministic approach is emphasized here. The second, kinetic Monte Carlo (KMC) simulation, incorporates statistical fluctuations, and is

widely used. The advantage of direct simulation is that all processes thought to be important can be included, but the corresponding disadvantages are that a) the rates of all such processes must be explicitly included, and b) the computational effort scales with the rate constant of the fastest process, typically adatom diffusion. The problem is even more acute for Molecular Dynamics (MD) simulations, where individual atomic motions are followed in real time. The Level Set (LS) method (Petersen *et al.* 2001, Ratsch *et al.* 2002) has been developed more recently. In particular, the LS method combines an atomic level description in the direction perpendicular to the substrate, with a deterministic continuum description in the substrate plane; it is therefore highly appropriate for investigating layer growth.

Any of these methods can be used to determine atomic-level parameters, or combination of parameters, which are needed to describe particular experimental results. Then, comparison of such parameters with *ab-initio* quantum theory is a reasonable goal, which has been achieved in a few cases. Once this circle has been closed we can be satisfied and move onto other problems. However, it remains a major challenge to do this in general. Crystal growth on substrates is an archetypal problem for *multi-scale modelling*, involving a large range of length and time scales. An individual method can only examine a very restricted subset of all such scales. In particular, the growth of quantum dots on (reconstructed, compound) semiconductor surfaces involves a whole series of reactions and potentially rate-limiting steps, which has presented a serious challenge to thorough analysis. We return to this topic in section 5. But first, in section 2, the progress that has been made in describing nucleation and growth using rate equations is described. Then, in section 3, nucleation on point defect sites is outlined; such defects can form the basis of a nanofabrication technique involving self-assembly. Section 4 deals with rate-diffusion equations in 1- and 2-dimensions, illustrated with recent experimental examples.

2. Rate equations and algebraic solutions

Rate equations are a natural starting point in the modelling of atomic, molecular and electronic processes. In the case of the processes discussed in the last section for cluster growth on surfaces, adatoms or ad-molecules are typically the mobile species, and we need to write down the rate equations for these species, and for their incorporation into clusters of all sizes and configurations. Needless to say, key simplifications are required to make progress.

A useful, but rather drastic, approximation is to divide the infinite set of rate equations into three sharp categories: first, for the single adatom areal density, which can be written

$$dn_1/dt = F(1-Z) - n_1/\tau, \text{ with } \tau^{-1} = \tau_a^{-1} + \tau_n^{-1} + \tau_c^{-1} + \dots; \quad (1)$$

here F is the deposition flux, (or equivalently the rate R), and Z the coverage of the substrate by stable clusters. The composite term n_1/τ represents all the loss terms, adsorption, nucleation, capture by stable clusters and maybe others (...), which add like resistances in parallel. The second is to consider the statistical mechanics of small clusters of size j , via the Walton relation (see Venables 1987, 1994, 2000). Then we can show that the corresponding rate equations for n_j are all effectively zero, and that n_j is proportional to n_1^j ; these represent sub-critical clusters, $2 \leq j \leq i$, where i is the critical cluster size. If $i = 1$ there are no such clusters or equations, at high super-saturation. Finally, all larger clusters ($j > i$) are deemed to be stable, and are grouped together as a density n_x in one further equation

$$dn_x/dt = U_i - U_c, \quad (2)$$

where the nucleation rate $U_i = \sigma_i D_1 n_1 n_i$, where σ_i is the relevant capture number, discussed further in section 4. The coalescence rate U_c has been expressed as $U_c = 2n_x dZ/dt$, although other forms become relevant at high coverage (Brune *et al.* 1999). The competitive nature of the processes discussed above is illustrated schematically in Figure 1 (Venables 1987).

The above simplifications mean that we have reduced our formulation to two coupled, non-linear, ordinary differential equations (ODE's) for n_1 and n_x . We now have two tasks, first to input a sensible set of processes. Capture by stable clusters is important in limiting nucleation, giving rise to the term τ_c^{-1} in equation (1); we can write this as $\tau_c^{-1} = \sigma_x D_1 n_x$. It is clear from this expression, and the schematic view of it in Figure 1, how the non-linearities arise; n_x depends on the $(j + 1)^{\text{th}}$ power of n_1 via equation (2), but n_x is also involved in limiting n_1 in equation (1). Depending on the processes that dominate, different regimes are expected, and if further processes are included (cluster mobility or mobility-induced coalescence for example), they may lead to different power laws, and different temperature dependencies. These points have long been appreciated in the literature (e.g. Venables 1973), and later examples may also be found via references quoted here.

The second task is to adopt a particular method of solution. We can simply integrate the differential equations, casting them in matrix form if appropriate; clearly we are not limited to two equations as above, but using more risks being unduly dependent on unknown parameters, which may or may not be included in a consistent fashion. These ODEs are stiff, and instabilities can easily result from using time or coverage steps that are too large. Some examples of direct integration are given in section 4.

A second possibility is to make a steady state approximation, in which all net rates of change are zero. For example, after an initial transient time, which is shorter than any of the individual times making up the overall τ in equation (1), dn_1/dt is effectively zero. Similarly, if we limit our attention to the maximum in n_x , dn_x/dt is also zero. Thus in this case, the ODE's reduce to non-linear coupled algebraic equations, for which we can obtain explicit or iterative solutions.

These algebraic solutions allow one to extract all the relevant material parameter dependencies within any one condensation regime, and are not limited to particular values of the critical nucleus size, i , as has been assumed by particular authors on particular occasions. The value of i is that value of an assumed j , which yields the minimum nucleation rate or density. During direct integration, this i -value can vary, thus including phenomena such as Ostwald ripening during deposition or annealing. In an algebraic solution, it is the value that produces the minimum density n_x , and so corresponds to the effective value for the deposition as a whole under the given conditions. The important point is that the critical nucleus size is an *output* of the calculation that has characteristic energies as *input*, not the other way around.

Modern computational packages can make these points conceptually clear. As illustrated in Figure 2, MatLab[®] 5.3 (Student edition) has been used to model the relatively complex surface reaction of Ti deposited onto Si(001) during the initial stages of forming titanium silicide, TiSi₂. This system has been investigated experimentally by several techniques, and Arrhenius (T^{-1}) and power law F -dependences are those expected for simple nucleation and growth models (McDaniels *et al.* 2001), with a small value of i in the range 2-6. The algebraic solution is formulated as a matrix in $[T^{-1}, j]$, which is simultaneously addressed to arrive at an iterative solution dependent on the three energies E_d , E_b (which is built up into E_j via pair-bond arguments), and E_a (which intervenes only at the highest T -values). In this case, we can get a perfect fit to a relatively small data set, with the energy values given in the figure, and the whole exercise takes less than a minute on a 300 MHz laptop computer. Algebraic solutions are very quick, *faster* than integrating ODE's, and *much faster* than KMC or LS methods. Thus they have an educative and summarizing value, provided that one accepts the conditions that lead to the formulation in the first place.

Does this mean that we believe the fine details of this model, as applied to the complex, reactive system $\text{Ti} + 2\text{Si} \rightarrow \text{TiSi}_2$? No, we do not: what figure 2 shows is that the RE pair-binding formulation is sufficiently flexible to provide an adequate 3-parameter fit to a limited data set, and that, in the situations illustrated, the supply of Si is not rate-limiting. It is

thought that Ti may diffuse as subsurface interstitials, creating mobile Si ad-dimers and immobile dimer vacancies. The late transition metals (Co, Ni, Pd, etc) dissolve into the bulk rather than re-evaporate (McDaniels *et al.* 2001), so E_a may not represent re-evaporation in this case. So the energy parameters, obtained by comparison of the model with experiment, are often lumped parameters, and may be open to interpretation. Moreover, one needs several sets of independent experimental data to test the model in detail, and these may not be easy to obtain. These points apply with even greater force when we consider extending the models beyond three energy parameters.

3. Extensions to defect nucleation

In many cases, particularly of metals deposited onto insulators, it has long been known that surface point defects and line defects such as surface steps act as preferred nucleation sites (see Venables 1994, 2000 for references). More recently this aspect has become of interest for nanofabrication, since well-defined and positioned traps are possible routes to self-assembly of nanostructures. Only point defect traps are considered here, which necessarily introduce two extra parameters, a trapping energy, E_t , and a trap density n_t . In the RE formulation, we also need to double-up the number of coupled equations, for the densities on traps, and on the terraces between the traps. This is illustrated schematically in figure 3(a).

Again we can make progress by focussing on the fate of the adatoms, in this case the trapped adatoms, with density n_{1t} , whose fate is governed by a rate equation of the form

$$dn_{1t}/dt = \sigma_{1t}D_1n_1n_{te} - n_{1t}v_d\exp(-(E_t+E_d)/kT), \quad (3)$$

where n_{te} is the number of empty traps $= n_t - n_{1t} - n_{xt}$. In steady state, this equation is zero, and inserting the usual form for $D_1 \sim v_d\exp(-E_d/kT)$, we deduce

$$n_{1t}/(n_t - n_{xt}) = A/(1+A), \text{ with } A = n_1C_t\exp(E_t/kT), \quad (4)$$

where C_t is an entropic constant, which has been put equal to 1 in the illustrative calculations performed to date. Equation (4) shows that the traps are full ($n_{1t} = n_t - n_{xt}$) in the strong trapping limit, whereas they depend exponentially on E_t/kT in the weak-trapping limit, as expected. This equation is a Langmuir-type isotherm for the occupation of traps; the trapping time constant (τ_t , in analogy to equation 1) to reach this steady state is very short, unless E_t is very large; but if E_t is large, then all the traps are full anyway.

The total nucleation rate is the sum of the nucleation rate on the terraces and at the defects. The nucleation rate equation without coalescence, analogously to equation (2), is

$$dn_x/dt = \sigma_i D_1 n_1 n_i + \sigma_{it} D_1 n_1 n_{it}, \quad (5)$$

where the second term is the nucleation rate on defects, and n_{it} is the density of critical clusters attached to defects, σ_{it} being the corresponding capture number. In the simplest case where the traps only act on the first atom which joins them, and entropic effects are ignored, we have

$$A_t = n_{it}/n_1 = (n_t - n_x)A/[n_1(1+A)]. \quad (6)$$

Typically, there are three regions: a high- T region where adatoms visit the traps but can become detached from them; a low- T region where the traps are full, but the nucleation density is largely unaffected, since $n_x > n_t$. In between, there is a plateau region where $n_x = n_t$; this plateau is longer if E_t is higher and E_d lower. The first requirement is obvious, and the latter is required so that adatoms reach the traps before finding each other. The plateau region is interesting for fabrication, since the resulting nanostructures are independent of processing conditions. A model calculation, originally intended for Fe/CaF₂ (Heim *et al.* 1996) is shown in figure 3(b).

This defect nucleation model contains several sub-cases, depending on values of the parameters. An interesting example is Pd/MgO(001), studied with atomic force microscopy (AFM) by Haas *et al.* (2000), where a single set of experiments has been analysed to put bounds on four energies; these data require a high trapping energy E_t and a low value of E_d , while also being sensitive to E_b and E_a , as illustrated in figure 4. In this case, the high temperature portion of the data corresponds to the transition to $i = 3$, so that individual adatoms remain attached to traps, but subsequent adatoms can become detached. These features are in agreement with calculations by Ferrari & Pacchioni (1996) and Venables & Harding (2000) for trapping of Pd in oxygen ion vacancies. The role of surface charges in stabilising both surface vacancies on insulator surfaces, and small clusters attached to such point defects, is very marked. Currently, different calculations agree that such effects are strong, but disagree on their exact magnitude; more comparative work is needed in this area.

Nucleation on defects has also been investigated using KMC simulations. An example is the work of Lee & Barabási (1998), who showed that an ordered array of defect trapping centers can lead to a markedly narrower size distribution than expected for randomly nucleated islands, but only when the mean diffusion length is comparable with, not much greater than, the distance between the defect traps. This corresponds to the upper end of the plateau regime, shown here in figure 3(b), where the adatom catchment area is roughly the

same as the regular Voronoi polyhedron around each defect site. The goal of a uniform size distribution is clearly desirable for applications; it may also be aided by stress and diffusion fields as discussed in the next two sections.

4. One- and two-dimensional rate-diffusion problems

The previous models have assumed spatial uniformity, and diffusion effects have been included implicitly via the effect on capture numbers. There are several problems where spatial correlations (adatom-adatom or adatom-cluster) have to be considered explicitly. For that we need to solve one or more diffusion equations in the relevant 1- or 2-dimensional geometry, in parallel with rate equations.

The most obvious problem concerns the value of the capture numbers themselves. Originally it was assumed that expressions for σ_1 , σ_i and σ_x (or σ_k in general) could be written down by inspection, as simply the number of sites around the periphery of the cluster, $2\pi(r_k+1)$ (Zinsmeister 1966), where the radius of the cluster in units of the jump distance is r_k . But a large effort by several authors showed that diffusion solutions, obtained by considering radial diffusion towards a typical k -cluster, were more realistic, and had Bessel function forms with an approximately logarithmic dependence on r_k (Venables 1973). As such it was often assumed subsequently that capture numbers can be approximated by constant values, especially for determining the dependence of densities such as n_x and n_1 on material parameters. But modern program suites such as MatLab[®] or Mathematica[®] contain library routines for Bessel functions, so it is easy to write in the correct diffusion forms. A more recent evaluation (Brune *et al.* 1999) has shown the extent of the differences between these forms, especially for the case of complete condensation and $i = 1$, which is appropriate for scanning tunneling microscopy (STM) experiments conducted at low temperatures.

Two sets of STM experiments have been conducted on the deposition and annealing of Cu adatoms at low temperatures (Repp *et al.* 2000, Knorr *et al.* 2002). After deposition and subsequent diffusion, the spatial distribution is non-random, and this feature has been analysed quantitatively to determine the oscillatory interaction between Cu adatoms at a function of radial separation. In the second of these experiments, Cu was deposited onto a Cu(111) substrate at 16.5K, to submonolayer doses ($\sim 3 \cdot 10^{-3}$ ML), followed by annealing at various temperatures around 20K for times up to 20 min. At short distances, there is repulsion between adatoms, and this repulsion forms a barrier to ad-dimer formation; but once formed, dimers are completely stable and do not diffuse. This system is therefore a fascinating case:

the ultimate quantum dot, a stable cluster of two atoms on a relatively smooth surface, formed by self-assembly. No quantum dot will ever be smaller than this!

However, these experiments also test capture number models, as a repulsive barrier of height E_B changes the form of the diffusion field around adatoms and clusters, and reduces the capture number markedly if $E_B/kT > 0.2$. As shown recently (Venables & Brune 2002), the full time-dependent form of the capture numbers is required to obtain agreement between RE solutions and KMC simulations in the earliest stages of low coverage (sub-ML) annealing. The diffusion solution is almost sufficient when the barrier is zero, but for finite barriers the diffusion solution is quite wrong, and the attachment-limited (barrier) solution, $\sigma_k = 2\pi(r_k+1)\exp(-E_B/kT)$ is much closer. Surprisingly, this is true even for barriers much smaller than the diffusion energy. Note also that this capture solution is similar to the form used by Zinsmeister (1966), but now reduced exponentially by the Boltzmann factor for the barrier. It corresponds to the case where there are no adatom-adatom or adatom-cluster spatial correlations prior to attachment.

The full solution for annealing, appropriate to Cu/Cu(111), is shown in figure 5. As a result of having the agreement between the KMC and RE solutions, we can extrapolate with confidence to other conditions, and compare with the experimental results of Repp *et al.* (2000) and Knorr *et al.* (2002). These results showed no dimer formation during 20 min at $\sim 17\text{K}$ and the completion of dimer formation after 20 min at 22K . As a result we were able to deduce that the barrier height E_B , or alternatively the repulsive energy maximum V_0 , for Cu/Cu(111), lies between 10 and 14 meV, as illustrated in figure 6. This figure is based on an integration of the rate equations for each V_0 value, up to the end of annealing (2 or 20 min) using the known E_d value, which is 40 ± 1 meV for Cu/Cu(111) (Knorr *et al.* 2002). The comparison with KMC simulations is again excellent, but the RE computation is much faster, < 10 min for each curve, versus many weeks for the KMC data. This again points to a role for RE solutions to summarize large amounts of computation done by other methods.

There are many other problems where 1- and 2-dimensional diffusion solutions are needed to complement rate equation treatments. These include capture by steps, the growth of quantum wires, deposition past a mask, and growth on anisotropic reconstructed surfaces. There is no space to discuss the first two topics; the last two are discussed next in relation to growth on (001) and (111) reconstructed semiconductor surfaces. We consider two examples: quantum dots formed from Ge/Si(001), and mask deposition of Ag/Si and Ag/Ge(111) as prototypical metal-semiconductor deposition and annealing systems.

5. Are semiconductors special?

Are semiconductors special? There are many possible reasons why they might be, although in some cases this may turn on questions of degree, not of kind. Due to intense interest in device applications, each individual system has been heavily studied. Different systems, which appear to be similar are often treated as being quite different by specialists. This can be traced to the interest in electronic and optical properties, with crystal growth mechanisms only appearing as a potential obstacle to growing films with the desired properties. The most obvious distinctions made are between a) indirect or direct band-gap materials (group IV versus III-V and II-VI's); b) the position of the conduction band minimum (e.g. Ge versus Si); c) the magnitude of the conduction and valence band offsets in hetero-structures. The role of strain, and alloying or clustering, on level shifts and splitting is also very important in relation to optical properties.

From a crystal growth viewpoint, complexities appear already with the surface reconstruction. The (2x1) and related superstructures on Si and Ge(001) arise from the strong dimer bonds which form to reduce the number of dangling bonds. As a result, most of the sublimation energy per atom, L , is gained on condensation by the formation of dimers (i.e. $(2E_a + E_{b2})$ per dimer in the notation of this paper), and very little extra energy remains to be gained when these dimers are incorporated into the growing crystal. This is consistent with the observation of a substantial density of ad-dimers at elevated temperature, with a low formation energy, E_{f2} , measured in quenching experiments as $E_{f2} = (2L - 2E_a - E_{b2}) = 0.35 \pm 0.05$ eV by Tromp & Mankos (1998).

The second complexity involves diffusion, where there are several competing mechanisms. Condensing adatoms compete to form dimers and/or join clusters, and diffusion itself is strongly anisotropic on the (2x1) surface, as is attachment to the different types of steps on this surface. Some of these mechanisms have been investigated quantitatively, most notably by atom-tracking STM (Swartzentruber 1996, see e.g. Venables 2000, chapter 7). Adatom diffusion energies, E_d , parallel to the rows have been measured both for Si (0.67 ± 0.08 eV) and Ge (0.62 eV), and also estimated perpendicular to the rows, at around 1.0 eV and 0.95 ± 0.1 eV respectively. Dimer diffusion energies, E_{d2} , have been measured on Si(001), and are around 1.1 eV parallel to the rows, with higher values reported (calculated or measured) both perpendicular to the rows, and in the troughs between the rows (Borovsky *et al.* 1997a, 1997b, 1999). Thus these surfaces present a highly complex energy landscape for diffusion, with different mechanisms active at various temperatures.

However, it is clear with the above energies that critical nuclei at practical growth temperatures may well be large, since the lateral binding (between strongly bound dimers) is so small. This feature has encouraged a ‘classical’ treatment of nucleation and growth in terms of edge energies for 2D nuclei; critical nucleus sizes up to $i = 650$ have been deduced in some circumstances (Thies & Tromp 1996). This approach has been reviewed recently by Tromp & Hannon (2002). These same energies show that, although the Si and Ge(001) growth systems may be close to 2D equilibrium, they are very far from equilibrium with their (3D) vapour, and re-evaporation is known to be negligible at normal growth temperatures, 450-650 °C. Using the known sublimation energy of Si, $L = 4.63 \pm 0.04$ eV, we can deduce from the Tromp group results that $(2E_a + E_{b2}) = 8.91 \pm 0.07$ eV. The dimer binding energy, E_{b2} , has been estimated theoretically as $E_{b2} = 2.0$ eV (Ramstad *et al.* 1995), so that adsorption energy of a Si adatom, E_a , must have a value close to 3.5 eV.

Most interest in Si, Ge and $\text{Si}_x\text{Ge}_{1-x}$ alloys has focussed on the growth of clusters above a wetting layer, which is of order 3ML thick for pure Ge grown on Si(001) (Krishnamurthy *et al.* 1991). The growth of such clusters has been intensively studied. Clusters take the form of rectangular huts, followed by domes of various shapes, all of which are coherent with the wetting layer; when the clusters are large enough, misfit dislocations are introduced and the clusters become incoherent. For application as quantum dots, such clusters need to be rather small, well within the coherent size limit. It has been found that the deposition temperature and flux play key roles, not just in determining nucleation densities, but also in determining the extent of surface- and inter-diffusion leading to alloying in the surface and subsurface regions.

Recently, very specific effects of the role of stress on diffusion and interdiffusion have been demonstrated in these systems. First, island formation is a response to the 4.2% mismatch between the Ge and Si lattice constants (less in the $\text{Si}_x\text{Ge}_{1-x}$ alloy system). Second, there is a large compressive stress, or equivalently elastic energy, at the edge of Ge-rich islands on the wetting layer. This region therefore has a higher chemical potential for diffusing Ge adatoms or dimers, which is higher for larger islands. At high enough growth temperature, this extra potential results in trench formation around domes, in which not only Ge but also Si diffuses away from the high stress region (Chaparro *et al.* 2000a).

Stress relief via interdiffusion also accounts for certain features of the hut-dome transition and the dome size distributions shown in figure 7. At 450°C the peak at 40nm diameter corresponds to coherent domes, and the peak at smaller sizes to huts, but

interdiffusion is not an important factor. At 600°C, the dome peak has shifted out to 80nm diameter, while a new broad peak has appeared centred at 40nm, which corresponds to partially alloyed huts. This hut to dome transition can thus be delayed to some extent via alloying at the higher growth temperatures. The sequence of shapes, the formation of trenches, and the introduction of dislocations have been documented in detail (Chaparro *et al.* 2000a) at a series of growth temperatures; the sequence at 600°C is shown in figure 8.

We are presently quite a long way from a fully quantitative model of all competing effects in this and similar systems: nucleation, growth (initial and stress-limited), ripening or coarsening, shape fluctuations and transitions, stress-influenced interdiffusion, and so on. But many pieces of the argument are in place. The high ad-dimer concentration and the small dimer-dimer interaction relates to the high critical nucleus size (small super-saturation) for nucleation and initial growth (Tromp & Hannon 2002). The high density of mobile species makes both Ostwald ripening and shape fluctuations relatively easy, as seen directly by *in-situ* low energy electron microscopy (LEEM) (Ross *et al.* 1998). Interdiffusion is strongly influenced by high stress concentrations at the edge of the clusters, and this effect leads to the trenches, with an effective diffusion coefficient that is considerably faster than bulk diffusion (Chaparro *et al.* 2000b, Denker *et al.* 2001).

Similar considerations apply to growth on Si(111), but here the reconstruction is the famous (7x7) structure, whose symmetry is triangular with a repeat distance of 2.688 nm. Adatoms form the mobile species, and the surface is rougher than (001), in the sense that there is a deep hole at the corners of the (7x7) cell and troughs along the dimerised edges, which separate the faulted and unfaulted halves of the cell. Thus diffusion on this surface represents a serious obstacle course; moreover growth of a second material, whether of a semiconductor such as Ge or metal such as Ag, reconstructs the surface differently. In the latter case the $\sqrt{3}$ (i.e. $\sqrt{3}\times\sqrt{3}R30^\circ$) structure, with ~ 1 ML coverage is especially stable, and growth and annealing at temperatures above 200°C take place on that surface, which is in effect an interface compound. Direct integration of the rate equations for Ag adatoms on both Si and Ge(111) has been used to obtain accurate values of adsorption, diffusion and binding energies on these surfaces (Venables *et al.* 1997), but again there are details left to sort out, notably those concerned with small particle mobility and interdiffusion.

At lower temperatures, there are kinetic limitations to the formation of the $\sqrt{3}$ structure, and this opens the possibility of manipulating the kinetics to obtain various types of quantum dots on the scale of the (7x7) structure. For example, several metal deposits on

Si(111) have been investigated by Wang & Lai (2001) and other authors; silicide nucleation and growth has been shown to be different on the faulted and unfaulted halves of the 7×7 unit cell (Bennett *et al.* 1994, Bennett & Von Känel 1999). It remains to be seen whether such structures can be developed further, or analysed effectively using the methods described here.

6. Discussion and conclusions.

A brief survey has been given of the use of rate and rate-diffusion equations to analyse experiments on nucleation densities during deposition and annealing. Extension of the simplest model to include nucleation on point defects is described, and computing accurate capture numbers has been revisited in comparison with KMC simulations. Experimental examples included metal-insulator, metal-metal, metal-semiconductor and elemental semiconductor growth systems, including those described as quantum dots. The growth of III-V and II-VI compound semiconductors has not been described, but these involve all the complexities discussed here, plus others of their own. In particular, the stages of surface reaction, partial interdiffusion leading to composition variation within the dot, are important in obtaining agreement with optical properties in III-V compounds (e.g. Shumway *et al.* 2002). An excellent example of multi-layer stacked quantum dots is in II-VI compounds (e.g. Raab *et al.* 2002), where impressive size and spatial uniformity has been demonstrated. These are good indicators of where the field is going, but are beyond the scope of this article.

One interesting item for future work is a comparison of these semiconductor and metal-semiconductor systems with the metal-metal systems discussed in the previous section. From the point of view of a large-scale description via rate equations, they are quite similar. The role of the stress is to change the energy landscape near the edge of the clusters, and so reduce the capture number for larger clusters. If the energies in the problem scale with the temperatures used in growth and annealing, and 600°C (873 K) for Ge/Si(001) is divided by a factor of 40, we find we are at 21.8 K, in the range of temperatures explored during annealing of Cu/Cu(111) in figure 5. The value of E_d for Cu/Cu(111) is 40 meV, and $40 \times (40 \text{ meV}) = 1.6 \text{ eV}$, somewhat higher, but of the same order of magnitude as that expected for Ge surface diffusion, and probably quite comparable for diffusion *within* the first layer or two.

The potential barrier for adatom attachment, interpreted in section 4 as $12 \pm 2 \text{ meV}$ for Cu/Cu(111) (Venables & Brune, 2002) translates into $0.48 \pm 0.08 \text{ eV}$, on multiplying by 40 to achieve the same effect in Ge/Si(001) at the higher temperature, all other things being equal. This of course, they are not, and factors of 40 in temperature are extreme

extrapolations. Nonetheless, the simple calculations of the energy landscape at the edge of quantum dots that have so far been performed, give energies around 0.2-0.4 eV (Drucker 1993, Barabási 1997, Enomoto 2001). On the other hand, the binding energy of dimer pairs, expected to be below 0.35 eV for Ge₂-Ge₂ on Si(001), becomes < 10 meV on dividing by 40, in contrast to a binding energy of order 0.3 eV expected for Cu adatom pairs. For example, Ovesson *et al.* (2001) have been interested in similar phenomena to those discussed here in section 4, and calculate $E_b = 0.26$ eV for Cu pairs on Cu(111). There are clearly other possible bases for comparison between such systems, which can be explored in future work.

There are similar analogies between silicide nucleation on Si and Ge(111) and metal-metal growth, e.g. Ag/Ag(111) and Ag/Ag(2ML)/Pt(111), where interface layers show misfit dislocation arrays, which act as a barrier to diffusion, and faulted or unfaulted halves of the surface cell, which act as preferential nucleation sites (Brune *et al.* 1998). The main relative difference between these widely different systems seems to be the large difference in critical nucleus size, or equivalently the tendency to Ostwald ripening during deposition and annealing, due to the relative difference of the lateral pair binding energy of the diffusing species. These are all example of quantities which can be easily varied, and explored rapidly with an RE treatment, and represent cases which may merit further study.

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Figure Captions

Figure 1: Schematic illustration of the interaction between nucleation and growth stages. The adatom density n_1 determines the critical cluster density n_i ; however, n_1 is itself determined by the arrival flux or rate (F or R) in conjunction with the various loss processes, which have associated characteristic times (τ_a , τ_n and τ_c) as described in the text (after Venables 1987, 2000).

Figure 2: Algebraic solution to rate equations for $E_a = 2.55$, $E_b = 0.7$, and a range of E_d values between 0.8 and 1.2 eV: a) temperature dependence for $F = 0.06$ ML/min; b) flux dependence for $T = 450^\circ\text{C}$. Pair-binding model for E_j up to $j = 3$, but with $E_3 = 2.2E_b$, rather than $2E_b$, which allows a range of $i = 2$ that would otherwise be absent (this range is longer the more E_3 is above $2E_b$). Extension to higher i -values might require higher values of E_a for comparable agreement at high temperature in panel a). Experimental nucleation densities for Ti/Si(001) are taken from McDaniels *et al.* (2001), and show agreement with $E_b = 1.1 \pm 0.1$ eV. See text for discussion.

Figure 3: a) Model for nucleation at attractive random point defects (density n_t), which can be occupied by adatoms (density n_{1t}), clusters (density n_{xt}) or can be empty; b) Algebraic solution to rate equations for trapping energy $E_t = 0.5$, $E_a = 1.16$, $E_b = 1.04$, and a range of E_d values between 0.1 and 0.6 eV. Originally for experiments on Fe/CaF₂(111) (Heim *et al.* 1996) recalculated for Venables (2000). See text for discussion.

Figure 4: Arrhenius representation of Pd island density N_x (cm⁻²) at 0.1 ML coverage on Ar-cleaved Mg(001): a) The solid line is the model for $E_d = 0.2$, $E_t = 1.5$, $E_b = 1.2$ and $E_a = 1.2$ eV, plus curves for $E_d = 0.3$ (dashed) and 0.4 eV (dotted lines), and experimental data from Haas *et al.* (2000). The insert shows the model for $i = 3$ applicable at high temperatures, using the same notation as figure 3a; b) Sensitivity to the parameter $E_b = 1.0$ (dashed) and 1.2 (full lines), with $E_a = 1.2$ eV important at high temperature, where the experimental data (triangles) indicate condensation to be incomplete (after Venables & Harding 2000). See text for discussion.

Figure 5: Predicted n_1 and n_x annealing curves as a function of $(D_1t)^{0.5}$, for annealing at 16.5 K with attachment barriers $E_B = 0, 5$ and 10meV , compared to KMC simulations. The capture numbers used are based on an interpolation scheme between attachment barrier and diffusion solutions, showing essential agreement with the KMC simulations. See text for discussion of how these curves apply to STM experiments on Cu/Cu(111). (Abstracted from Venables & Brune 2002).

Figure 6: Predicted annealing curves as a function of barrier height V_0 , at temperatures $17 < T_a < 23\text{K}$. Plotted is the ratio $(n_1 + n_x)$ after a 2 minute anneal, divided by the initial value $n_{\text{tot}} = (n_1 + n_x)$ after deposition. These curves use the time-dependent capture number expression as in figure 5. The curves for 19 and 21K are also compared with the KMC simulations. Additionally a curve for annealing at 22 K for 20 minutes is given. See text for discussion of how these curves apply to STM experiments on Cu/Cu(111). (Abstracted from Venables & Brune 2002).

Figure 7: Size distributions of Ge/Si(001) islands grown at 450 and 600°C to coverages indicated. For each temperature, the left-hand peak corresponds to huts, while the right-hand peak corresponds to domes. At 600 and 650°C (not shown), large alloyed hut peaks exist between the two outer peaks; these large hut peaks are not present at 550 (not shown) and 450°C. Note also that the dome peak shifts to larger sizes at higher growth temperatures. The existence of large, alloyed huts and the shift of the dome peak to larger sizes is indicative of Si interdiffusion. Formation of a lower misfit alloy allows clusters to attain larger sizes prior to shape transitions of dislocation introduction. (after Chaparro *et al.* 2000a).

Figure 8: Summary of shape evolution of Ge clusters grown at $F = 1.4 \text{ ML/min.}$ onto Si(001) at 600°C. The vertical position of the horizontal bars represents the contact angle of the dominant facet with the (001) substrate. The horizontal extent of the bar represents the size range over which that morphology exists. The top half of the figure shows the evolution of the $\langle 110 \rangle$ cross section and the bottom half the $\langle 100 \rangle$ cross section. (after Chaparro *et al.* 2000a).