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Reaction kinetic model of height selection in heteroepitaxial growth of quantum dots

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Abstract. A reaction kinetic model is proposed for height selection of heteroepitaxially growing nanometer-thick quantum dots. The model describes the growth by a set of rate equations for the combined size and height distributions of the dots. In addition to nucleation and growth, the model includes a coarse-grained conversion rate incorporating kinetics of height changes. With suitably chosen rate coefficients the model reproduces qualitatively the experimentally observed height-selected size distributions and their evolution. The results support the view that the height selection and the form of the size distribution both result from the oscillating energy barrier for the transformation of dots of different heights, and this transformation barrier is considerably larger in magnitude than oscillations in the electronic energy due to quantum well states in the dot.

PACS. 81.07.Ta Quantum dots – 68.65.Hb Quantum dots – 68.35.Md Surface thermodynamics, surface energies

1 Introduction

Quantum dots (QDs) have been a subject of much research effort during the last decade due to their potential use for novel technological applications. Recent advanced surface probing techniques have been able to resolve the equilibrium shapes of the QDs and the electronic properties of optimal-sized dots (see e.g. Refs. [1–3]). A case of particular interest is the formation of tower-shaped structures in deposition of Pb on Si(111) [4,5] or Cu(111) [6,7]. The height selection observed in these cases has been assigned to the quantum size effect (QSE), where certain QD heights are favored due to minima in the confinement energy of electrons as a function of the QD height. There are also experiments which have reported a related phenomena of stability of layer heights due to quantum confinement on Pb/Si(111) [8] and Pb/Cu(111) [9], and also charge oscillations as a function of height [10]. The origins of the size-selection is by now well understood owing to many studies focused on the electronic properties of QDs, which thus forms the first step toward understanding the controllability and applicability of a single QD [3,11].

In the modeling of self-assembled growth of nanostructures the knowledge of energetics is yet a starting point. Recently, there has been much progress in modeling the growth and decay of nanostructures by the so-called step models, where surfaces are treated as step-like geometric structures on which the adatoms move. In these models, the key quantities are the step chemical potential, governing the detachment and attachment of adatoms, and the interlayer mass transport [12,13]. The step models have been quite successful in explaining the basic features of nanostructure growth, particularly in case of the shape preserving morphologies and their scaling properties [12,13], but also in the constrained evolution, where shape transformations are due to mass redistribution in the evolving structures [14]. In addition, also the continuum models of nanostructure growth have advanced considerably and are now able to give insight on the evolution of the morphology as well as spatial ordering of QDs [15–17].

The few existing kinetic models which can be applied to describe the Stranski-Krastanov growth of QDs are those of Dobbs et al. [18], Koduvely and Zangwill [19], and Heyn [20]. Dobbs et al. concentrated on growth of semiconducting material by considering the average densities of adatoms and 2D and 3D clusters. In their model adatom attachment and detachment are treated in a self-consistent way, and the 3D clusters are formed from the 2D ones with the strain-dependent conversion rate. Koduvely and Zangwill [19] generalized the approach of Dobbs et al. [18] by including adatom detachment from 2D and 3D dots and

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and taking the dot-dot interactions into account in a phenomenological way. They remark, however, that it is difficult to obtain the size distributions due to a large number of coupled differential equations (which in the present case form a stiff problem for numerical integration). Heyn [20] introduced rate equations for the size distributions, but he considered only the distributions in the base area and separately the evolution of the average adatom density on top of 2D dots. However, the kinetics of the height selection in growth of QDs and consequently the evolution of the size distribution when height selection occurs is still a less understood subject, and at present there is no model which reproduces the experimentally observed QD size distribution and its evolution in case of QSE.

2 The model

We describe here a reaction kinetic model for calculation of the size distribution and height selection of QDs, formed by the Stranski-Krastanov growth in presence of wetting layer. In particular, we focus on the case of height-selected QDs as recently realized experimentally as Pb structures grown on Si(111) [4,5] and Cu(111) [6,7] surfaces. To this end, we model QD formation (in its 3D-growth phase) with a resolution of one monolayer. The reaction kinetic model describing the transitions between different QD heights should in addition to the height changes describe also the growth of the structures in the lateral direction. The model takes therefore into account adatom attachment into a QD (of any height) increasing also the QD base area A, nucleation of new dots of height one (dimers), and the QD height conversion from h to $h+1$ decreasing the base area in the process. We assume that all QDs have circular base areas given by $A = V/h$, where V is the total volume of the QD (i.e. the total number of atoms s times the atomic volume). During the conversion event the base area and the height change such that $A \to Ah/(h+1)$ thus keeping the total number of atoms constant. The conversion event is assumed to proceed more rapidly than any other event corresponding to the approximation that the relaxation events leading to a new equilibrium configuration are instantaneous. In order to keep the model as simple as possible at this stage, we have left out e.g. adatom detachment and downward conversion $h \to h-1$, but they can be incorporated into the model. The corresponding set of rate equations are:

$$\frac{dn_1}{dt} = F(1-\theta_0) - 2D\sigma_1 n_1^2 - Dn_1 \sum_{s,h>1} \sigma_s^{(h)} n_s^{(h)}; \quad (1)$$

$$\frac{dn_s^{(h)}}{dt} = \gamma_s^{(h-1)} n_s^{(h-1)} - \gamma_s^{(h)} n_s^{(h)} + F\theta_0 (n_{s-1}^{(h)} - n_s^{(h)}) + D\sigma_{s-1}^{(h)} n_1 n_{s-1}^{(h)} - D\sigma_s^{(h)} n_1 n_s^{(h)} + 2D\sigma_1 n_1^2 \delta_{2,s}, \quad (2)$$

where n_1 is the adatom concentration in the first layer, $n_s^{(h)}$ is the distribution of QDs with mass $s \geq 2$ and height $h \geq 1$ (so that the base area of the dot is $A = s/h$), F the deposition flux, θ_0 the surface coverage (area covered by the QD bases) and D is the adatom diffusion coefficient. The effective rate for the transition $h \to h+1$ is given by rate coefficient $\gamma_s^{(h)}$. The rate coefficient for adatom detachment to dot with size s and height h, the so called capture numbers (compare with Refs. [18–20]), are given by $\sigma_s^{(h)}$ for dots with base area $A = s/h$. It should be noted that the first term $F(1-\theta_0)$ in equation (1) and the third term in equation (2) take into account the fact that when dots are formed and grow large enough, most of deposition flux impinges directly into QDs and does not increase the adatom concentration on a surface. Thus direct deposition increases only the total mass of a QD. The effect of wetting layer on growth is of no direct importance here, so we have assumed throughout the calculation that adatom coverage of wetting layer is 1 ML (compare Eqs. (1), (2) with corresponding Eqs. (1), (2) in Ref. [20]). The set of rate equations are in some respects similar to those used previously by Heyn [20], also to those introduced by Dobbs et al. [18] and Kodulevy et al. [19], but the major difference is now that our equations (1), (2) span the whole configuration space of sizes s and heights h on equal footing.

Next we specify the rate coefficients which contain the input parameters of the model. The capture numbers are chosen to be related to the geometry through the base are $A = s/h$ of the island so that

$$\sigma_s^{(h)} = (s/h)^{\mu}, \quad (3)$$

where $\mu = 1/3$ correspond to three dimensional dots. Now $\sigma_1 \equiv \sigma_1^{(h)}$ gives the capture number of a single adatom. Since our final goal is to model height oscillations in QD formation, a reasonable choice is an oscillating energy barrier for upward conversion rates $\gamma_s^{(h)}$. The upward conversion rate for $h = 1$ is given by

$$\gamma_s^{(1)} = \pi r^2 \exp\left[\frac{E_i + (2E_e - E_0 \log(A)/\sqrt{A}}{k_B T}\right], \quad (4)$$

where $r = \sqrt{A/\pi}$ is the radius of a dot with base area $A = s/h$ and the strain parameters for the first layer $E_i = 1.0$ eV, $E_e = 0.17$ eV, $E_0 = 3.28$ eV are taken from reference [18]. For the heights $h > 1$ the upward conversion rate is given by

$$\gamma_s^{(h)} = \pi r^2 \exp\left[\frac{-E_b[1 - \cos(2\pi(h-1)/H)]}{k_B T}\right], \quad (5)$$

where parameters are otherwise similar as in equation (4) but now $E_b = 0.50$ eV is the effective energy barrier for upward conversion, and H is the period of barrier oscillations. The value for E_b is chosen so that the height distribution and its oscillations resemble qualitatively the experimentally observed situation within a reasonable temperature range. Therefore, the parameters are not chosen for a specific system, but rather to show that values in overall agreement with typical values for different systems can reproduce the generic behavior of dot growth.

The choice of an oscillating conversion rate $\gamma_s^{(h)}$ requires further discussion. On Pb/Si(111) it has been shown by ab initio calculations that the total electronic energy of a QD oscillates with an amplitude of 15 meV [7]. On Pb/Si(111) recent experiments indicate differences between even and odd layer heights [21]. Using ab initio calculations this is addressed to diffusion barrier oscillations roughly at even or odd height quantum dots with a small oscillation amplitude [21]. Also, in the case of nanowires preferred wire configurations have been proposed to emerge due to quantum confinement effects leading to an oscillating conductance and charge distribution [22]. On the other hand, on Pb/Si(111) the measurements [4] indicate the effective activation barrier for a transition between 5 and 7 layer QDs to be of the order of 0.3 eV. Thus, although in the microscopic level the barrier for such transformations is related to energetics of the quantum well states, the barrier which is most useful for describing the growth of the structures is rather an effective barrier for mesoscopic structure transformations. Moreover, the conversion rate includes the temperature-dependent strain term only for the first layer. It is straightforward to include a strain-dependent activation energy in $\gamma_s^{(h)}$ for $h > 1$, and contribution from QD-QD interactions [19]. At present, there is no coarse graining method, which produces a prediction for such a mesoscopic transformation barrier, but the present model pins-down its expected magnitude, needed to explain the growth kinetics.

3 Results

Instead of direct integration, it is advantageous to solve the rate equations using the particle coalescence method (PCM) [23–25], where all adatoms and clusters are kept in a list containing their sizes. Since spatial information is neglected, there is no need to construct a physical lattice. Each event has its corresponding rate, for example for adatom attachment events we have the total rate $\Gamma_{\mathrm{Att}} = \sum_i \Gamma_i$, where Γ_i is the adatom attachment rate for the QD of size i. To choose an event, we use a rejection-free Monte Carlo algorithm [26], which allows us to choose a successful event at every simulation step.

At low temperatures, the upward conversion rate in our model is much slower than the attachment rate for adatoms onto dots. Thus, in this regime the conversion rate (probability for transition $h \to h+1$) can be omitted and growth proceeds as in the usual irreversible case. QDs nucleate but grow only in lateral size when coalescence is not included. Since at high coverages the deposition flux increases the size of the dots, the average base area grows linearly for $\theta \gg 1$ ML. This reflects the fact that at low temperatures growth proceeds in a layer-by-layer mode in agreement with experiments [9]. However, at higher temperatures the conversion rate becomes important. As 2D dots get larger, they begin to convert into 3D structures due to size-dependent part in the conversion rate. This leads to the saturation of the average area, since a dot with a large enough base area has a high probability to convert into a multilayer structure reducing the base area in the process. These results are illustrated in Figure 1, which shows the temperature dependence of the average base area of a dot $\langle A \rangle$ as a function of the (total) deposited coverage θ between $T = 300$–500 K corresponding to $\mathcal{R} = D/F = 10^5$, where D is the adatom diffusion coefficient. The base area is defined as the area that a dot occupies on a surface. The behavior is rather regular as a function of coverage, resembling the scaling behavior of the island growth. Assuming such scaling in form $\langle A \rangle \sim \theta^\beta$ it is possible to extract the exponent $\beta \approx 0.79$ measured from the initial part of the data. This value happens to be close the growth exponent $\beta = 2/(3-2\mu)$ calculated in submonolayer growth of islands with capture rate given by equation (3) [27]. Here, we used $\mu = 1/3$ in the adatom attachment rate which gives $\beta = 6/7 \approx 0.85$, which is close to extracted value $\beta \approx 0.79$. However, in present case this is more a suggestive conjecture than an exact result, because the base area of dots we are dealing with is limited to sizes too small to allow defining reliable scaling results. More important than the scaling are the following qualitative notions: (1) at low temperatures the average base area grows roughly linearly for large enough coverages since most of adatoms coming from deposition flux impinge directly into existing dots; (2) at high temperatures the average base area saturates when the conversion begins to dominate and this saturation value depends on temperature such that larger the temperature, smaller the saturation value of $\langle A \rangle$. Finally, the inset shows the total dot densities as a function of coverage, where it can be seen that (3) at lower temperatures the QD density is smaller than at high temperatures since the average base area is larger.

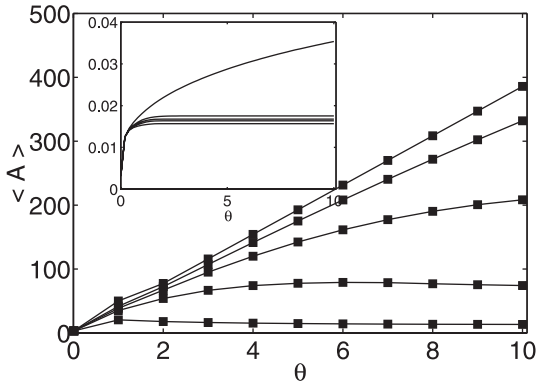

Fig. 1. The average base area as a function of deposited coverage at temperatures $T = 300$, 350, 400, 450 and 500 K (from top to bottom). The inset shows the corresponding total QD densities (from bottom to top). Note that when temperature is high enough, the QD density increases monotonically.

These results for the average base area and the total density of dots are in agreement with Heyn [20] and Dobbs et al. [18]. Heyn found a saturation of the dot size corresponding to the maximum of the size distribution as a function of coverage. The saturation value is reached after the size decreases from the maximum value, in agreement

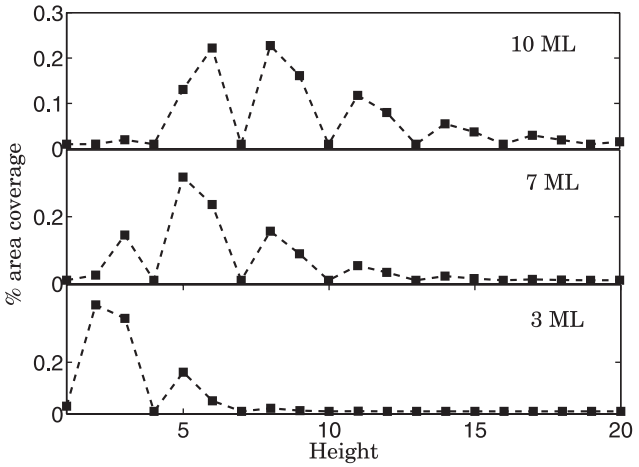

Fig. 2. The height distribution at $T = 500$ K and $\theta = 3$, 7, and 10 ML (from bottom to top). The distribution corresponds to the number of quantum dots with height h covering a certain fraction of the surface.

with our results (see the high temperature curves in Fig. 1). The density of 3D dots also levels off as the coverage approaches 2 ML (maximum coverage in Ref. [20]), thus indicating saturation regime at higher coverages. Our simulations show the saturation of the 3D dot density as a function of coverage also found by Dobbs et al. [18].

Experimentally, the most striking aspect of the heteroepitaxial Pb QDs is the height selection as discussed in the introduction. Our model is capable of reproducing height oscillations in 3D growth at high temperatures. In Figure 2 the height distribution is shown at $T = 500$ K as a function of the deposited coverage $\theta = 3$, 7, and 10 ML, and using the oscillation period $H = 3$ for the upward conversion rate $\gamma_s^{(h)}$. The period is clearly seen in the figure where the distance between the peaks is H layers. As expected, the height distribution broadens as the coverage increases. At large coverages the deposition flux increases the sizes of the existing quantum dots and thus the number of low dots is small. We find that the term $F(1-\theta_0)$ in the equation for the adatom density is crucial in the sense that it suppresses nucleation of new dots at large coverages. With a constant flux term F only, the height distribution always develops a tail at small heights. These oscillations are in qualitative agreement with the experiments on Pb/Cu(111) [6].

The emergence of height oscillations is directly related to the oscillating barrier of the conversion rate $\gamma_s^{(h)}$ (which denotes the probability for transition $h \to h+1$). If a constant barrier is used instead, the oscillations disappear and only a single-peaked height distribution is observed. The amplitude of the barrier oscillations E_b for $\gamma_s^{(h)}$ affects only quantitative results; using $E_b = 0.3$ eV the height oscillations appear already at $T = 300$ K, but the form of the height distribution is the same. The same applies also to the average base area. In the strain-dependent part of $\gamma_s^{(h)}$ the most crucial parameter is E_i which denotes the nucleation barrier for the critical dot size i to form (here we have used $i = 1$). For values $E_i \ll 1.0$ eV the first layer dot density has larger values than for $E_i \approx 1.0$ eV. In all cases, however, the form of the height distribution is robust. Therefore, the final conclusion is that in order to have the height selection, effective barrier for conversion between different heights needs to be a magnitude larger than the characteristic energy scale of energy oscillation in quantum well states. However, this is to be expected because the barriers involved in the present model are energy barriers for mesoscopic transformations of the whole structures. It remains a further theoretical challenge to relate such barriers to microscopic energy oscillations of quantum well states through controlled coarse graining procedures.

We have additionally checked the robustness of our results by modifying the conversion rate such that the strain part takes the same form for every layer, in which case the oscillation pattern does not considerably change in form as temperature increases, but the height distribution only extends into larger values for given coverage. We have also included downward conversion into the model such that the QDs can decrease their height with a similarly oscillating rate $\tau_s^{(h)}$ for downward conversion. Irrespective of whether $\tau_s^{(h)}$ is in- or out-of-phase with respect to the upward rate $\gamma_s^{(h)}$ the density of QDs having height $h > 1$ is very low. Thus, in the view of the present model it seems that downward conversion does not play any role in the formation of QD height oscillations during growth. However, their role becomes crucial during relaxation period when the flux is turned off.

4 Conclusions

In summary, we have developed a reaction kinetic model for the growth of nanostructures and evolution of their size distribution. The model includes the relevant generic processes into a rate equation model, which can be efficiently solved by Monte Carlo methods. In particular, we concentrate here on the scenario of an oscillating energy barrier controlling the upward mass flux along the sides of the growing QD. Our results suggest that this could be the key factor explaining the experimentally observed height oscillations and the associated evolution of size distribution on Pb/Cu(111) and bilayer growth on Pb/Si(111). In particular, our results for the height distributions are in qualitative agreement with height oscillations observed in the Pb/Cu(111) system [6] with minimal number of processes included in the model. In addition of reproducing the size distributions, the results support the conclusion that the energy scale for height selection is much larger than oscillations in the electronic energy due to quantum well states in the dot.

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