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Size calibration of epitaxial islands via a two-step growth protocol: Kinetic Monte Carlo and effective-medium theory study

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The kinetic Monte Carlo technique has been used to simulate irreversible growth of epitaxial islands in two consecutive steps. At the first step a small quantity of adatoms was simultaneously deposited at the surface at random positions and allowed us to freely diffuse until nucleating new islands or until being caught by the earlier nucleated ones. It was found that the distribution of the Voronoi cell (VC) areas around the island centers could be accurately described by the Gaussian distribution (GD) which was narrower than the GD describing the VCs of randomly distributed nucleation centers. Thus, our simulations provide an alternative explanation of the narrowing that was observed experimentally and attributed to elastic forces. At the second step the surface was exposed to an atomic deposition flux that was chosen to be small enough for the nucleation of new islands was strongly suppressed and the growth was dominated by the aggregation of deposited atoms into existing islands. At this step the island size distributions (ISDs) obtained could be also well described by the GD only more peaked than the corresponding VC area distributions. The narrowing has been explained in the framework of an effective medium theory. In several cases the simulated VC area distributions and ISDs semi-quantitatively agreed with those observed experimentally. Furthermore, the two-step growth made the island diameter distributions much more symmetric than those obtained under the conventional irreversible growth setup. It is suggested that this technique may provide a method of controlled growth of the island ensembles with narrow and symmetric size distributions in practically any system: homo- or heteroepitaxial.

1. Introduction

In mass fabrication of surface nanoislands for engineering purposes a major task that is to control the characteristics of the island ensembles essential for the intended functionality. Sophisticated techniques of the controlled epitaxial growth based on the substrate patterning have been developed in the semiconductor industry [1]. They, however, became very costly and/or inefficient at the lower end of the nanoisland sizes $\lesssim 10$ nm [2]. But islands in this size range are of considerable practical interest. For example, in optoelectronics the quantum size effect that allows for the control of the photoluminescence wavelength of the quantum dots (QDs) is operative only in QDs of such sizes [3,4]. In chemistry, the highest catalytic efficiency of metallic clusters is often achieved for the islands a few nanometers in diameter [5]. Besides, smaller QDs allow reducing the sizes of QD-based devices [6]. Therefore, there exists a need for development of controlled growth techniques that are efficient at this scale.

In the past two decades considerable efforts have been devoted to the study of phenomena of self-assembly and self-organization of QDs via the Stranski–Krastanov growth mode during strained epitaxy on flat substrates [3,4]. Good size calibration and ordering of QDs seen experimentally in some systems made them to be of considerable interest for engineering applications [1,2]. The Stranski–Krastanov growth, however, takes place under conditions close to thermodynamic equilibrium [3,7,8]. In this case many complex processes of atomic exchange between the QDs, the substrate and the wetting layer are taking place in the system, so sophisticated modeling is needed for their accurate description [9,10]. Because currently such modeling is not yet sufficiently predictive, the control of the thermodynamically limited QD growth is not an easy task. For example, such a basic quantity as the average size of islands in the QD ensemble is difficult to control even with the use of the substrate pre-patterning [11].

In contrast, when the growth is irreversible (or kinetically controlled [7]), that is, when the detachment of atoms from the islands is strongly suppressed, the average island size can be easily controlled via the quantity of the deposited material (the surface coverage) [12]. But the size uniformity of the islands under the conventional experimental setup is very poor with the full width at half maximum of the ISD being approximately equal to the average island size. Besides, in contrast to the symmetric ISDs of the Stranski–Krastanov QDs, the irreversibly grown ISDs are very asymmetric [12].

The aim of the present paper is to suggest a two-step setup of the irreversible growth which would allow for the self-assembly (i. e., in the absence of any substrate pre-patterning) of epitaxial islands with narrower and more symmetric size distributions than under the conventional growth technique [12].

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In the conventional growth set-up the atoms are deposited at a constant rate in one uninterrupted deposition run (or step) on an initially clean surface. The islands in this kind of growth nucleate when two diffusing monomers meet at the nearest neighbor sites (the so-called $i = 1$ case [12]). Such nucleation is called homogeneous. It continues till the end of the deposition at diminishing but not negligible rate which is responsible for the high relative density of the islands of small and intermediate sizes.

It was predicted theoretically [13] that if on the surface there exist some foreign nucleation centers at which the *heterogeneous* nucleation and subsequent growth predominantly take palace, i. e., when the homogeneous nucleation is negligible, the corresponding ISDs became more symmetric because of the reduced density of small islands in comparison with the homogeneous case. In the absence of nucleation the growth is governed by the island capture zones (CZs)—the regions on the substrate that supply individual islands with the mobile monomers [13–18]. It can be shown that in this case the ISDs should reproduce the CZ distributions (CZDs) [13,19] with only some broadening due the statistical fluctuations of the number of atoms in smaller islands [17].

In [13,19,20] it was pointed out that some partial order in the positions of the nucleation centers would lead to the narrowing of the CZDs [12,21] but practical ways of controlling the order on unpatterned substrates were not suggested. Narrow CZDs and ISDs were indeed observed in several experiments but only their qualitative explanations were suggested, such as a possible influence of elastic and/or of long-range repulsive forces [15,22,23].

In the present paper we will show that there exist purely kinetic mechanisms of both the creation of partial order among the nucleation centers and of the narrowing of the ISDs in comparison with the area distributions of the corresponding "geometric" CZs (the VCs and/or edge cells [21]). The two-step growth protocol will be explained in the next section and illustrated with the kinetic Monte Carlo (KMC) simulations. In Section 3 we will discuss the narrowing of the ISDs with respect to the geometric CZDs observed in the KMC simulations in the framework of a mean field-like effective medium theory. In the last section we will present our conclusions.

2. KMC simulations

In the lattice gas model of irreversible growth, when two freely diffusing monomers meet on the nearest neighbor sites they nucleate a stable dimer island with the rate that can be characterized by the so-called capture number σ_1 (see [12], $i = 1$ case). A straightforward mean-field estimate on the square lattice which we used in the simulations gives the value $\sigma_1 = 12$ [24]. Analytic solution [25] and the KMC simulations [24], however, give considerably smaller values. This may be caused by the quick disappearance of nearby mobile monomers due to the nucleation. Because of this, at later stages of the growth the monomers effectively avoid each other which mimics their repulsion. This is reflected in the small value of σ_1 which is proportional to the monomer pair correlation function (see Eq. (46) in [24]). In our opinion, this provides a mechanism for the appearance of the hard-core correlations [20,23] among the nucleation centers. The mechanism is similar in nature to the correlations arising due to the depletion zones around the islands [12].

To proceed farther, a digression about our terminology is in order. Everywhere we, following [13,17] and other authors, call "heterogeneous" the nucleation of the islands at the centers that can irreversibly bind the mobile monomers and that exist before the start of the main deposition run. The homogeneous nucleation, in contrast, takes place when the monomers meet each other. In the proposed two-step growth procedure the growth centers are prepared at the first step and they need not consist of atoms that are different from those deposited at the second step, though this is a legitimate alternative. So for simplicity, we used identical monomers at both steps of our simulations. The difference with the homogeneous case was in the island density. Even when the nucleation centers consist of atoms of the same kind as the deposited monomers, if their density is substantially higher than the island density that would grow at a given total coverage under the conventional one-step growth, then the homogeneous nucleation would be strongly suppressed and the aggregation on the islands of approximately constant density would take place. In these terms the nucleation of the minute islands at the first step is *homogeneous*, while the further growth of the islands at the second step follows the *inhomogeneous* nucleation.

A possible experimental set-up is as follows. A necessary quantity of the monomers is deposited on a clean surface at random positions. We note that this can be achieved in different ways: as a fast deposit at a low temperature when the atomic mobility can be neglected, but also via heating to high temperature to produce necessary quantity of thermally excited and weakly correlated (because of the high temperature) vacancies [16] and/or free monomers. Then the temperature either raised or lowered (in the second case) and the monomers perform a random walk on the surface until nucleating at their meeting new islands or being attached to already existing ones. The minute islands thus obtained serve as the nucleation centers at the second growth step.

2.1. Nucleation of growth centers

To realize the first growth step in the KMC simulations we first deposited a small quantity (characterized by the coverage $\theta_0 \ll 1$) of immobile monomers on a clean surface. We assumed that the substrate temperature is so low and/or that the deposition is so fast that the monomer mobility during the deposition could be neglected. Next the monomers were allowed to diffuse until caught within islands. The heating or cooling schedules were irrelevant because in the absence of the deposition flux the only scale for the kinetics is the diffusion rate, its precise temperature dependent value being irrelevant.

Following many authors (see, e. g., [12,13,19,22]) we characterized the partial order in the spatial distribution of the growth centers by the probability distribution of the sizes of the Voronoi polygons surrounding each center (the VCs). To quantitatively characterize the order, use has been made of the value of the shape parameter β of the rescaled gamma distribution fitted to the VC area distribution

$$g(A) = \frac{1}{A_{\text{av}}} G_\beta(u = A/A_{\text{av}}), \tag{1}$$

where

$$G_\beta(u) = \frac{\beta^\beta}{\Gamma(\beta)} u^{\beta-1} e^{-\beta u}, \tag{2}$$

A is the VC area and A_{av} its average value. The rescaled distribution satisfies the normalization conditions

$$\int_0^\infty G_\beta(u)du = \int_0^\infty G_\beta(u)udu = 1.$$

The quality of the fit can be seen in Fig. 5 in Section 3 from a typical simulated VC areas data shown by the "times" symbols.

The results of the simulations are shown in Fig. 1 for values of θ_0 within the range ~$2 \cdot 10^{-4}$–$6 \cdot 10^{-3}$. As is seen, fitted values of β monotonously grew in the range $\beta_{VC} \simeq 5.8 - 6.3$ [22] which is appreciably larger than the value $\beta_{VC} = 3.6$ for completely disordered impurities found in [13,19]. Thus, for purely kinetic reasons we obtained enhanced value of β similar to those seen experimentally in [22] where the spatial correlations between the nucleation centers were explained by the influence of elastic forces.

The average sizes of islands s^0_{av} for all simulated coverages were approximately equal to 2.75 atoms (within 1% scatter). This means

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