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Universality in size distributions of irreversibly grown epitaxial islands: Kinetic Monte Carlo simulations and the rate equations study

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The scaling approach to the irreversible epitaxial growth gained wide recognition due to its ability to describe with the use of a universal function the island size distributions (ISDs) corresponding to a broad range of experimental conditions. The approach, however, is operative only in the case of large average island sizes s_{av} and large diffusion to deposition rates ratios R. Physically this corresponds to long deposition times and/or high temperatures. We argue that the ISDs exhibit yet another universality property which holds for much broader range of growth conditions, in particular, for low temperatures (small R) and small s_{av} (short deposition times). We show that the normalized ISDs corresponding to the same s_{av} are accurately described by the same universal distribution.

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Epitaxial growth is considered to be a promising tool for the fabrication of nanostructures of technological interest.[1–3] Because the growth at the surface is an inherently nonequilibrium phenomenon,[3] the understanding of underlying microscopic kinetics is key to the development of efficient engineering techniques. The kinetics, however, are very complex, judging, e.g., from the complexity of the nanostructures they produce.[3] Because of that, their theoretical study is currently restricted to simple models, such as the model of irreversible growth (IG).[2,4]

The IG model describes the growth of islands on a crystal surface in terms of a few simple kinetics. The deposition is described by random creation of atoms at the surface at the rate characterized by a homogeneous flux F. After the landing, the atom may meet previously deposited atoms either immediately or after some number of intersite hops performed at a constant rate h. In both cases the atom gets attached either to another mobile atom—in which case a new island is nucleated—or to an existing island. The attachment is supposed to be *irreversible*, i.e., the atom cannot leave the island to which it belongs. Rearrangement of atoms within the islands, however, is allowed. These rearrangements may change island morphologies from ramified dendritelike appearance at low temperatures to compact polygonal shapes at high temperatures in case of monolayer-high islands [the case of two-dimensional (2D) growth][5] up to various three-dimensional (3D) morphologies if the hopping and nucleation on the tops of 2D islands are allowed.[1] Because the intraisland kinetics are usually system specific and in general are poorly known, considerable popularity gained the approach which avoids detailed description of these kinetics by focusing mainly on some *universal* features of the IG common to all epitaxial systems. This approach has been based on the ideas of scaling.[4,6–15] Central to it is the expression for the island size distribution (ISD),

$$N_s = (\theta/s_{av}^2)[f(s/s_{av}) + O(1/s_{av}) + \cdots], \tag{1}$$

where N_s is the density of islands of size s, θ the coverage, s_{av} the average island size, and f the scaling function. The second term in the brackets is our estimate of the error introduced by the replacement of the discrete differences with respect to the island size $s=2,3,\ldots$ in the mean-field rate equations (REs) of the type of Eq. (6) below by the continuous derivatives $\partial/\partial s$. This replacement is a major approximation made in derivation of Eq. (1).[11,12,16] For the functions of the scaling variable $x=s/s_{av}$, such as f in Eq. (1), the approximation of the derivative $\partial f/\partial x$ by the finite difference (and vice versa) introduces the error of order of the step size, or $O(1/s_{av})$ in our case (we assume that the error in the RE leads to similar error in the solution). Finally, by dots in Eq. (1) we denoted the corrections to f due to the terms omitted in the RE used in the derivation.

Thus, according to Eq. (1) the scaling is expected to hold in the case of large islands ($s_{av}\to\infty$).[16–18] Besides being large, the islands should not coalesce which in the case of physical extended islands restricts the coverage to small values of $\theta \lesssim 0.2$.[4,18] Further, the scaling analysis shows[4,16–18] that in 2D

$$s_{av} \simeq \theta^{2/3} R^{1/3}, \tag{2}$$

where

$$R = h/F. \tag{3}$$

With coverage θ being small, from Eq. (2) it is seen that the only way to get large s_{av} is to perform the growth at large R. Because of the cubic root in Eq. (3), the dependence of s_{av} on R is not very strong. For example, to increase the average island size three times, R should be enlarged almost thirtyfold. So to make the $O(1/s_{av})$ term in Eq. (1) negligible, quite large values of R are needed. E.g., in Ref. 18 an approximate scaling was found for $R \geq 10^7$, while in Ref. 19 the exact scaling was not found even for R as large as 10^9. Because increasing R by reducing the flux F in Eq. (3) would require simultaneous prolongation of the deposition time, more practical is to increase h by raising the temperature.[8,9,20] Therefore, large-R deposition would normally correspond to high-temperature growth.

Thus, the scaling approach is operative only in the case of large islands and high-temperature growth, while small islands and/or low-temperature growth[21–23] are currently being described with the use of the kinetic Monte Carlo (kMC) simulations and the RE.[18] These approaches, however, require knowledge of microscopic kinetics which are poorly known, especially when the phenomena responsible for the reversibility are of interest. The latter can be generically defined as those which allow the atoms detach from the islands.[24,25] Their study should provide us with a clue to the mechanisms of growth of the nanostructures of practical interest, such as the periodic arrays of size-calibrated islands known as the quantum dots.[3] Because the islands grown during the IG are of very different sizes and are randomly scattered over the surface,[1,4,6–11,13–15] it is the reversible growth and accompanying it phenomena that could be responsible for the growth of the quantum dot arrays.

A major advantage of the scaling approach is that its use does not require any knowledge of microscopic kinetics, provided the growth remains irreversible. The parameters F, h, R, and θ (we will call them the growth parameters) are varied externally, while s_{av} and f entering Eq. (1) can be found from the measured ISD N_s. As long as the growth remains irreversible, the scaling functions obtained at different temperatures should coincide. Deviations from the scaling at high temperatures mean that irreversible phenomena begin to influence the ISD. These deviations can be used to assess and quantify these phenomena without any explicit knowledge of the microscopic kinetics.[8,9,20,26]

The aim of the present Rapid Communication is to propose a universality principle similar in the spirit to the scaling approach but which would be applicable at all temperatures and all island sizes. The analog of Eq. (1) in our approach plays the equation

$$N_s = N\rho(s, s_{av}), \tag{4}$$

where N is the total islands density

$$N = \sum_{s\geq 2} N_s = (\theta - N_1)/s_{av} \approx \theta/s_{av} \tag{5}$$

and ρ the normalized ISD: $\Sigma_{s\geq 2}\rho(s, s_{av}) = 1$.

Similar to Eq. (1), Eq. (4) contains only experimentally observable quantities. The difference is that instead of one universal function $f(s/s_{av})$ of the scaling theory, in our approach we have a one-parameter family of functions $\rho(s, s_{av})$, if the second argument is treated as a parameter. This lesser universality in the ISD shapes is compensated by the fact that Eq. (4) is expected to adequately describe the ISD at all admissible values of the growth parameters and at all average island sizes, including very small ones. Because the number of island sizes s over which the deposited atoms are distributed grows in proportion to s_{av} (see Figs. 1 and 2), for large values of s_{av} good statistics is hard to gather. For example, with the same total statistics as in large-s_{av} experiments of Ref. 8 at $T=207$ °C, in the $s_{av}=3$ case the statistics per island size would be about 40 times better (see Fig. 1) and this without any restraints on the growth temperature or its duration.

To substantiate our approach we will use the conventional

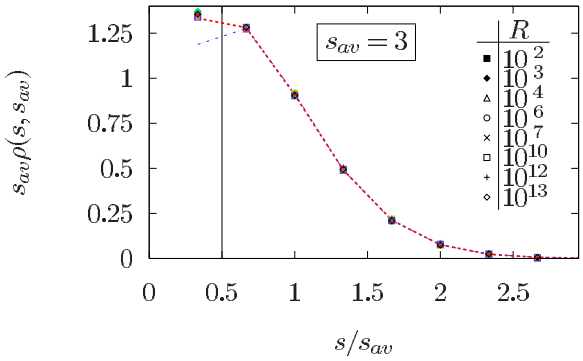

FIG. 1. (Color online) Points to the right of thin vertical line: the normalized ISD for different values of $R=h/F$; points to the left of the line: rescaled density of mobile monomers; dashed line: solution of the rate Eqs. (6) for point islands ($\sigma_s=1$); and dashed-dotted line: the Poisson distribution normalized to $s_{av}=3$. The statistics were gathered over 15–30 kMC simulation runs.

tools used in theoretical studies of the surface growth: the mean-field RE and the kMC. In Refs. 2, 4, and 11–13 Eq. (1) was derived as an approximate asymptotic solution of the RE. It is remarkable to note that our Eq. (4) satisfies the RE *exactly*. This is most easily seen if the REs are cast in the form proposed in Ref. 7,

$$\frac{d\hat{N}_1}{d\hat{\theta}} = 1 - 2\sigma_1\hat{N}_1^2 - \hat{N}_1\sum_{s\geq 2}\sigma_s\hat{N}_s, \tag{6a}$$

$$\frac{d\hat{N}_s}{d\hat{\theta}} = \hat{N}_1(\sigma_{s-1}\hat{N}_{s-1} - \sigma_s\hat{N}_s), \quad s \geq 2, \tag{6b}$$

where $\hat{N}_s \equiv R^{1/2}N_s$, $\hat{\theta} \equiv R^{1/2}\theta$, and σ_s are the capture numbers. Equations (6a) and (6b) will coincide with Eq. (12) of Ref. 7 after substitution,

$$\sigma_s = s^p, \tag{7}$$

where for small island sizes good approximations are considered to be $p=0$ for point islands, $p=1/2$ for compact islands, and p equal to the inverse fractal dimension for ramified islands (see Ref. 7 and references therein). For large islands more sophisticated models have been proposed. For ex-

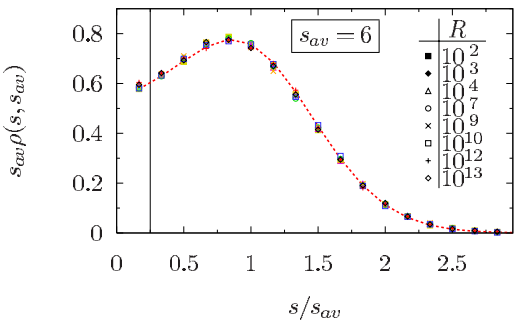

FIG. 2. (Color online) Same as in Fig. 1 for $s_{av}=6$ but without the Poisson distribution which at this value of s_{av} significantly deviates from the data.

ample, in Ref. 14 it was found that for large point islands σ_s should grow linearly with $x=s/s_{av}$ for $x \geq 1$; in Ref. 25 a quadratic dependence on x was substantiated. With the initial condition $\hat{N}_s=0$ at $\hat{\theta}=0$, the solution of Eq. (6) for all these choices of σ_s will depend only on s, s_{av}, and the evolution parameter $\hat{\theta}$. But $s_{av}(\hat{\theta})$ grows monotonously with $\hat{\theta}$, so the inverse function $\hat{\theta}(s_{av})$ can be introduced. Hence, $\rho=N_s/N=\hat{N}_s/\hat{N}$ is a function of only s and s_{av}, which proves the validity of Eq. (4) at the mean-field level.

It is to be noted that RE (6) is not exact. For example, it neglects the direct impingement terms corresponding to deposition of atoms on island tops. These terms have a power-law dependence on coverage and at small θ are also small.[13] To assess the influence of the neglected terms on the universality we, following established routine,[4–7,10–15,17,19,26] compared the RE predictions with the kMC simulations in which the direct impingement was treated exactly. In Figs. 1 and 2 an excellent agreement between the RE predictions and the kMC simulations of the point-island model on the square lattice can be seen. To facilitate comparison with other simulations we plot the data using the scaling variables: s/s_{av} as the abscissa and the scaling function $s_{av}\rho$ as the ordinate [cf. Eqs. (4) and (5) with Eq. (1)]. As is seen, the size distributions are identical within the statistical uncertainty for all values of R studied.

The simulations were performed with the use of the accelerated kMC algorithm appropriate for large low-density systems which we developed recently.[27] Detailed explanation of the algorithm and its explicit application to the one-dimensional (1D) growth can be found in the above paper. Here we only point out two essential simplifications brought out by the rectangular geometry in the 2D case. First, because the hops along two orthogonal directions are independent, probability distribution of the boxed atoms has a separable form

$$p_{2D}(\vec{i},t) = p(i_x,t)p(i_y,t), \tag{8}$$

where $p(i_{x,y},t)$ is the solution of the 1D problem explicitly given by Eq. (4) of Ref. 27. Because the probability for the boxed atom to leave the box is equal to half the sum of the probabilities over the box perimeter, from Eq. (8) and from the normalization $\Sigma_i p(i,t)=1$ it follows that this probability is twice the function $P_{\text{end}}(t)$ of Ref. 27. So the time-dependent rate of the system evolution is given by formula (7) of Ref. 27 with the hopping part (the last two terms) multiplied by two.

The point-island model was chosen in order to facilitate the kMC simulations (the model is being widely used in the field mainly for this reason). From the RE analysis above, however, it can be seen that the universality should hold for extended island models as well. This is confirmed by the kMC simulations in Ref. 27 where in Fig. 3 one can see an excellent agreement between the ISDs for extended 1D islands simulated for three values of $R=10^6$, 10^9, and 10^{12} at coverages $\theta=0.1$, 0.01, and 0.001, respectively. From the scaling relation $s_{av} \propto (\theta^3 R)^{1/4}$ (see Ref. 4) follows that the values of s_{av} were approximately equal.

The most important property of the universal distributions shown in Figs. 1 and 2 is that they can describe ISDs at small values of R where the scaling approach cannot be used even for large islands. In Fig. 1 additionally is shown the Poisson distribution which corresponds to the deposition of immobile atoms ($R=0$). The excellent agreement of the Poisson ISD with the kMC shows that in the $s_{av}=3$ case the universality holds down to very small values of $R \to 0$. In the case $s_{av}=6$ shown in Fig. 2, however, the Poisson distribution (not shown) is quite different from the simulation data. We ascribe this to the fact that, as can be seen from Fig. 3, for $R \lesssim 10^2$ the coverage would exceed one monolayer, while admissible values of theta are $\theta \lesssim 0.2$.[4]

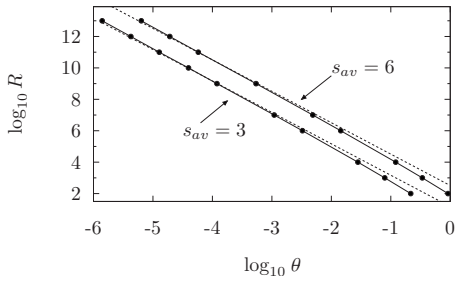

FIG. 3. Solid lines: the contour lines corresponding to constant values of the function $s_{av}(\theta,R)$. The lines are drawn through the pairs of R and θ values (solid circles) obtained in the kMC simulations. The dashed lines are calculated on the basis of the rate Eq. (6).

The ISDs obtained in our simulations qualitatively agree with the low-R ISDs presented in Fig. 6(a) of Ref. 18 as well as resemble some ISDs from Refs. 28 and 29. This latter similarity, however, is accidental; in Sec. 3.3 of Ref. 18, it was stressed that the low-R behavior is distinct from the asymptotic behavior found in Refs. 28 and 29.

To conclude, in this Rapid Communication we substantiated a universality principle obeyed by the ISD during irreversible epitaxial growth which is exact at the level of mean-field rate equations and also agrees within small statistical errors with the exact kMC simulations. The principle states that the normalized ISD remains invariant under such changes in growth parameters that leave the average island size s_{av} unaltered. In this respect our approach is similar to the scaling theory which additionally establishes connection between ISDs corresponding to different s_{av}. The scaling, however, takes place only at asymptotically large values of s_{av} and of the hopping to deposition rates ratio R while the universality holds at all allowable values of the growth parameters. So we expect that the use of the universality in interpretation of experimental data will lead to easier identification and quantification of reversibility phenomena than the approaches based on the scaling theory which currently is being used for this purpose, as explained below. Quantitative description of the reversibility phenomena is important from technological point of view as they contribute to the growth of regular nanostructures of practical interest.

From experimental standpoint, we see the following advantages of our approach. (i) In contrast to scaling approach, there is no need in enhancing R by increasing the temperature and/or by slowing down the deposition—thus jeopardizing the growth irreversibility. The universality may hold at

any values of these parameters and can be observed during fast deposition at low temperatures when the irreversibility is easier to maintain. (ii) In our approach the growth time can be strongly reduced because, in contrast to the scaling approach, it does not require that islands were large. This, *inter alia,* makes our approach applicable to the cases when only very small islands are of interest, as, e.g., in the metallic surface-catalytic systems where the efficiency of the catalyst strongly depend on the size of the atomic clusters in the range of three to ten atoms.[21,22] The scaling approach cannot be applied in such cases. Furthermore, (iii) with small islands one can gather much better statistics with the same effort than in the case of large islands because there is less island sizes corresponding to nontrivial values of the ISD function. In our opinion, these advantages outweigh the necessity to grow island ensembles with the same s_{av} to have identical ISDs. From the log-log contour plot in Fig. 3 it is seen that the pairs of values of R and θ corresponding to the same s_{av} lie on the curves with very small curvature, so the linear interpolation should be quite efficient. This technique was used in our kMC simulations.

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[1] H. Brune, Surf. Sci. Rep. **31**, 125 (1998).
[2] C. Ratsch and J. A. Venables, J. Vac. Sci. Technol. A **21**, S96 (2003).
[3] J. V. Barth, G. Costantini, and K. Kern, Nature (London) **437**, 671 (2005).
[4] M. C. Bartelt and J. W. Evans, Phys. Rev. B **46**, 12675 (1992).
[5] G. S. Bales and D. C. Chrzan, Phys. Rev. B **50**, 6057 (1994).
[6] T. Vicsek and F. Family, Phys. Rev. Lett. **52**, 1669 (1984).
[7] J. G. Amar, F. Family, and P.-M. Lam, Phys. Rev. B **50**, 8781 (1994).
[8] J. A. Stroscio and D. T. Pierce, Phys. Rev. B **49**, 8522 (1994).
[9] T. R. Linderoth, J. J. Mortensen, K. W. Jacobsen, E. Lægsgaard, I. Stensgaard, and F. Besenbacher, Phys. Rev. Lett. **77**, 87 (1996).
[10] C. Ratsch, A. Zangwill, P. Šmilauer, and D. D. Vvedensky, Phys. Rev. Lett. **72**, 3194 (1994).
[11] D. D. Vvedensky, Phys. Rev. B **62**, 15435 (2000).
[12] P. A. Mulheran and D. A. Robbie, Europhys. Lett. **49**, 617 (2000).
[13] M. N. Popescu, J. G. Amar, and F. Family, Phys. Rev. B **64**, 205404 (2001).
[14] M. C. Bartelt and J. W. Evans, Phys. Rev. B **54**, R17359 (1996).
[15] J. G. Amar and M. N. Popescu, Phys. Rev. B **69**, 033401 (2004).
[16] J. W. Evans and M. C. Bartelt, Phys. Rev. B **63**, 235408 (2001).
[17] J. W. Evans and M. C. Bartelt, Phys. Rev. B **66**, 235410 (2002).
[18] M. C. Bartelt, J. B. Hannon, A. K. Schmid, C. R. Stoldt, and J. W. Evans, Colloids Surf., A **165**, 373 (2000).
[19] C. Ratsch, Y. Landa, and R. Vardavas, Surf. Sci. **578**, 196 (2005).
[20] S. Günther, E. Kopatzki, M. C. Bartelt, J. W. Evans, and R. J. Behm, Phys. Rev. Lett. **73**, 553 (1994).
[21] A. Herzing, C. Kiely, A. Carley, P. Landon, and G. Hutchings, Science **321**, 1331 (2008).
[22] S. Lee, C. Fan, T. Wu, and S. L. Anderson, J. Chem. Phys. **123**, 124710 (2005).
[23] B. Müller, L. Nedelmann, B. Fischer, H. Brune, and K. Kern, Phys. Rev. B **54**, 17858 (1996).
[24] G. S. Bales and A. Zangwill, Phys. Rev. B **55**, R1973 (1997).
[25] F. Gibou, C. Ratsch, and R. Caflisch, Phys. Rev. B **67**, 155403 (2003).
[26] H. Brune, G. S. Bales, J. Jacobsen, C. Boragno, and K. Kern, Phys. Rev. B **60**, 5991 (1999).
[27] V. I. Tokar and H. Dreyssé, Phys. Rev. E **77**, 066705 (2008).
[28] A. Zangwill and E. Kaxiras, Surf. Sci. **326**, L483 (1995).
[29] J. G. Amar and F. Family, Phys. Rev. Lett. **74**, 2066 (1995).