Impact of Substrate Defects on the Equilibrium One-dimensional Island Size Distribution

D.A. Mirabella and C.M. Aldao

Reprinted from

Adsorption Science & Technology

2011 Volume 29 Number 6

Multi-Science Publishing Co. Ltd.
5 Wates Way, Brentwood, Essex CM15 9TB, United Kingdom

Impact of Substrate Defects on the Equilibrium One-dimensional Island Size Distribution[†]

D.A. Mirabella and C.M. Aldao[*] *Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), Juan B. Justo 4302, B7608FDQ Mar del Plata, Argentina.*

(Received 30 April 2011; accepted 2 June 2011)

ABSTRACT: As long as only first-neighbour interactions are considered, equilibrium island size distributions of monoatomic islands in one dimension follow an exponential law regardless of the strength and the repulsive or attractive character of the adsorbate–adsorbate interactions. However, one-dimensional atomic wires obtained via nucleation at the step edges have a monomodal island size distribution. In this paper, we present a simple one-dimensional Monte Carlo model that shows how the monomodal distribution observed experimentally can be obtained by including surface defects that only suppress the interaction between two successive adsorbates.

1. INTRODUCTION

Sub-monolayer growth is usually two-dimensional, but in some cases it can be effectively one-dimensional. Indeed, step structures at metal and semiconductor surfaces are employed in molecular beam epitaxy as deposition templates to produce one-dimensional atomic wires (Owen *et al*. 2006). Due to the increase in binding energy at step sites, adatoms deposited on vicinal surfaces can self-assemble chain-like structures at steps (Iguain *et al*. 1998; Chen and Boland 2004; Albao *et al*. 2005). The size and separation of atomic wires can be controlled by adjusting the average step edge separation and adatom coverage. These self-assembled nanostructures are of outstanding importance for the fabrication of microelectronic devices (Meixner *et al*. 2005). Due to its technological relevance, investigations of such systems have become an active research field involving the theory of nucleation in one dimension, atomistic diffusion and epitaxial growth.

In many cases, island formation can be explained using energetic principles and equilibrium thermodynamics (Daruka and Barabási 1997; Barabási 1999). Germanium grown on a Si(001) substrate is a good example. As the system is annealed, the island size distribution approaches a saturation value corresponding to the equilibrium configuration. Although partially annealed configurations show rather strong non-equilibrium features, once they are fully annealed, the size distribution of the islands is in excellent agreement with the predictions of equilibrium theory (Kamins *et al*. 1997; Mereiros-Ribeiro *et al*. 1998; Ross *et al*. 1998).

In other cases, island formation clearly exhibits non-equilibrium features and then dynamical models must be invoked. In molecular beam epitaxy (MBE) at low temperature, island formation and evolution in the sub-monolayer regime regularly involves deposition, diffusion, nucleation, aggregation and coalescence of islands — processes that proceed irreversibly (Amar *et al*. 1994a,b, 2001; Jensen *et*

[†] Published in the Festschrift of the journal dedicated to Professor Giorgio Zgrablich on the occasion of his 70th birthday and to celebrate his 50 years as a faculty member at the National University of San Luis in Argentina.

[*] Author to whom all correspondence should be addressed. E-mail: cmaldao@mdp.edu.ar.

al. 1994). In this paper, we will focus on one-dimensional systems under equilibrium conditions and, in particular, on the consequences of defects on the island size distributions.

Exact solutions of equilibrium island size distributions, when only first-neighbour interactions between adsorbates are included, have been derived by determining all possible configurations of the system (Yilmaz and Zimmermann 2005; Vavro 2001). Also an approach based on mass action law was successful in reproducing the size distribution at the low-coverage limit (Priester and Lannoo 1995). Using a thermodynamic approach, Gambardella *et al*. (2006) derived an analytical expression for the island size distribution, calculating the island free energy as a function of the island step energy, the adsorption energy, the chemical potential and the configurational entropy. More recently, we presented an alternative derivation of the theoretical equilibrium island size distribution, by resorting to the detailed balance principle (Mirabella and Aldao 2011) which reproduces the results obtained previously (Priester and Lannoo 1995; Gambardella *et al*. 2006). In this approach, the island size distributions can be easily derived from transition rates between islands of different sizes, these rates being determined by particle interaction energies and the geometric constraints imposed by the transition.

The steps are not completely straight experimentally, but they usually present kinks that act as defects altering the adsorbate–adsorbate interactions. In this paper, we extend the Monte Carlo simulation recently presented to understand how step defects can modify the island size distribution (Mirabella and Aldao 2011). We have found that including surface defects in our simulation changes the behaviour of the island size distribution from an exponential to a monomodal shape when first-neighbour interactions between adsorbates are present, without resorting to more complicated mechanisms such as repulsive far-distant neighbour interactions due to surface stress (Mirabella and Aldao 2011; Tokar and Dreyssé 2003, 2007). Kinetic effects can also lead to a monomodal form of the island size distribution in a system out of equilibrium (Amar *et al*. 1994; Jensen *et al*. 1994). However, it is our goal to show that a monomodal form can be obtained in a system under equilibrium conditions without resorting to long-distance interactions.

In order to check the validity of our model, we have derived an analytical model to calculate island size distributions for non-interacting adsorbates, with and without defects, to compare with MC simulations. Also, we present an analytical model when adsorbate–adsorbate interactions are included and defects are periodically distributed. We found that this model reproduces the Monte Carlo outcomes.

2. EQUILIBRIUM ISLAND SIZE DISTRIBUTION FOR NON-INTERACTING PARTICLES IN A SUBSTRATE WITH AND WITHOUT DEFECTS

In this section, we develop a simple analytical approach to obtain the island size distribution including substrate defects. We start by considering a set of particles distributed at random on the defect-free substrate. In this model, the probability of finding a single-particle island as a function of coverage is given by $\theta(1 - \theta)^2$. Similarly, the probability of an island being formed by two particles is $\theta^2(1 - \theta)^2$. Following this argument, it is possible to derive an expression for the island concentration of size n, c_n, as:

$$c_n = \theta^n(1 - \theta)^2 = c_1\theta^{n-1} \tag{1}$$

Kinks along steps have been taken into account in our model by suppressing the interaction between two successive adsorbates as shown in Figure 1 overleaf. In the present calculation, in

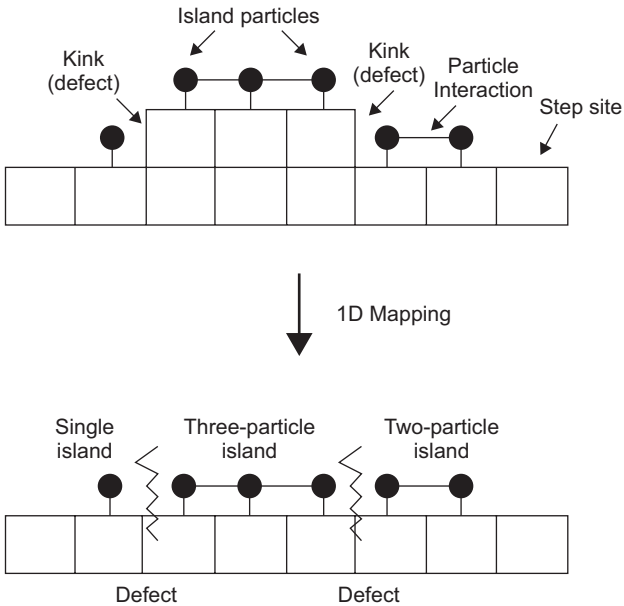

Figure 1. Schematic describing the interactions considered in modelling adsorbates at step edges and the influence of defects. Squares represent substrate particles and circles represent adsorbate particles. The upper drawing shows islands formed by neighbouring adsorbate particles. Note that a kink at the step nulls the interaction between neighbouring adsorbate particles. The lower drawing shows the one-dimensional mapping of the step edge. Note that the effect of kinks is maintained by not including interactions between neighbouring adsorbate particles. Neighbouring adsorbate particles are not considered to form part of the same island if a kink is in between.

which inter-adsorbate interactions are not present, defects simply break the space in a set of boxes (independent sub-systems) limiting the island size that can be formed.

Following the same argument as in the zero-defect model [equation (1)], the probability of finding a single-particle island in the presence of defects can be determined straightforwardly. To do this, we define the density of defects D as the ratio between the number of defects and the number of lattice sites, N/L. Consistently, D can be interpreted as the probability of having a defect between two neighbouring particles. In the presence of defects, the probability of finding a single-particle island can be calculated by considering the different possible alternatives of having a single occupied site close to two empty sites, an occupied site close to an empty site and a neighbour site occupied with a defect in between, and finally an occupied site with occupied neighbours and defects in between. Then, the resulting single island concentration is

$$c_1 = \theta(1 - \theta)^2 + 2D\theta^2(1 - \theta) + D^2\theta^3 = \theta(1 - \theta + \theta D)^2 \quad (2)$$

The extra term (θD) in equation (2), in comparison with equation (1), accounts for the fact that island ends are not only established by empty sites but also by defects between neighbouring adsorbates.

Extending this reasoning, we can calculate the n-particle island concentration as a function of the adsorbate coverage θ and defect concentration D as:

$$c_n = \theta^n(1 - D)^{n-1}(1 - \theta + \theta D)^2 = c_1[\theta(1 - D)]^{n-1} \quad (3)$$

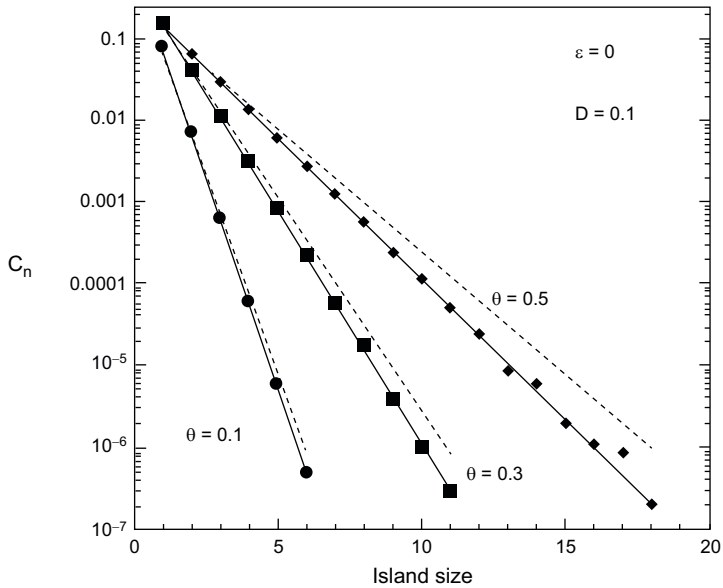

Figure 2. Island size distributions for non-interacting particles with a defect density D = 0 and 0.1 and coverages θ = 0.1, 0.3 and 0.5. Symbols correspond to Monte Carlo results and fitted lines correspond to equation (3) for D = 0.1. Dotted lines correspond to distributions for a step without defects, D = 0. Defects reduce the island average size but the distributions maintain their exponential character. For example, for θ = 0.5, the average island size becomes ca. 9.1% smaller.

As can be seen in equation (3), substrate defects alter island size distributions by breaking large islands into small ones, which affects the exponential shape of the distributions by only changing their slopes. In Figure 2, we show the effects of a defect concentration D = 0.1 on island size distributions for three different coverages, and in Figure 3 the consequence of an increasing density of defects for a constant coverage θ = 0.3. The results obtained by means of equation (3) were tested with Monte Carlo simulations.

3. EQUILIBRIUM ISLAND SIZE DISTRIBUTION FOR NEAREST-NEIGHBOUR INTERACTING PARTICLES WITHOUT DEFECTS

The statistical distribution of interacting particles for a 1D substrate can be derived using thermodynamic arguments. Under thermal equilibrium, the general reaction can be expressed as

$$N_n = N_{n-1} + N_1 \tag{4}$$

This equation accounts for the formation of an island of size n when a single particle attaches to a cluster of size n − 1. In particular, assuming an attractive interaction ε between first-neighbour particles, resorting to the mass action law we can write:

$$\frac{c_n}{c_{n-1}c_1} = \exp(\varepsilon/kT) \tag{5}$$

This expression is similar to the one obtained by Priester and Lannoo (1995) using the law of mass action and is valid in the low-coverage limit. Equation (5) can be easily re-written to obtain an expression for the island density that depends only on ε and c_1:

$$c_n = c_1[c_1 \exp(\varepsilon/kT)]^{n-1} \tag{6}$$

Equation (6) is a decreasing geometric series of the type $c_n = c_1 x^{n-1}$. From this expression, the density of islands k and the coverage θ can be determined without difficulty as:

$$k = \sum_n c_n = \frac{c_1}{1 - x} \tag{7}$$

$$\theta = \sum_n n c_n = \frac{c_1}{(1 - x)^2} \tag{8}$$

Thus, $x = (\theta - k)/\theta$ and $c_1 = k^2/\theta$, and the island size distribution can be written as:

$$c_n = \frac{k^2}{\theta}\left(\frac{\theta - k}{\theta}\right)^{n-1} \tag{9}$$

Substituting $c_n = N_n/N$, $k = K/N$ and $\theta = M/N$, equation (9) can be re-written as:

$$N_n = K^2(M - K)^{n-1}M^{-n} \tag{10}$$

where the island size distribution is expressed in terms of the number of adsorbed particles M and the number of islands K — equation (12) in Gambardella *et al.* (2006) — allowing for a direct comparison with experiment.

Equations (6) and (9) are decreasing geometric series, independent of the coverage and energy strengths, even when attractive inter-particle interactions are considered. At first sight, this analytical result is counter-intuitive because, for large attractive interactions, larger energetically more stable islands would form at the expense of small ones. As the energy increases and the number of small islands is reduced, the entropy is still responsible for maintaining the monotonically decreasing character of the island distribution. On the other hand, experimental observations have shown that the resulting island size distributions are monomodal. In the next section, we discuss the possibility of obtaining equilibrium monomodal distributions by including surface defects in the simulation.

4. RESULTS AND DISCUSSION

Monte Carlo simulations were carried out using an array of 10^4 sites that simulated the support on which the particles are deposited, i.e. the step. Particles were initially distributed at random and periodic boundary conditions were used to avoid edge effects. The equilibrium configuration for the system was obtained following the standard method of Metropolis. Thus, two sites, i (occupied) and j (unoccupied), are selected at random. The energy of the configuration is calculated. A virtual transfer of a substrate particle i to site j is considered and the energy for the new configuration is calculated and compared with the energy of the initial configuration. If the

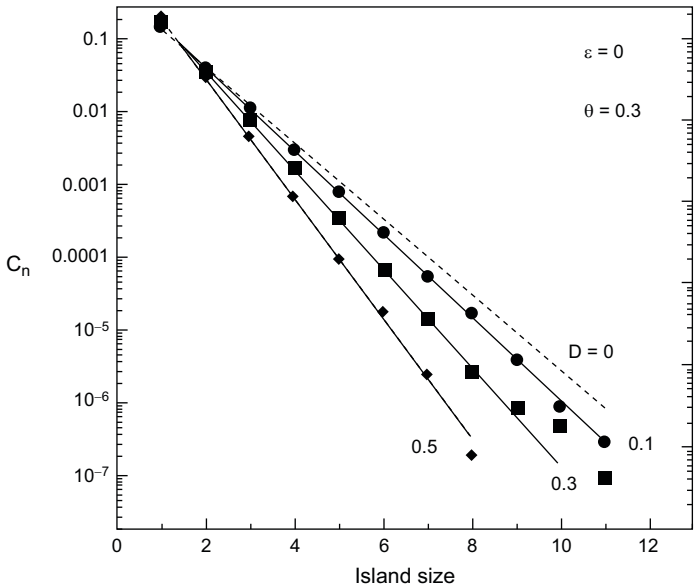

Figure 3. Island size distributions for non-interacting particles for a coverage $\theta = 0.3$ and defect density $D = 0$, 0.1, 0.3 and 0.5. Symbols correspond to Monte Carlo results. Full lines correspond to equation (3) while the dotted line corresponds to the distribution for a step without defects. Defects reduce the island average size but the distributions maintain their exponential character. For $D = 0.5$, the average island size decreases by ca. 18%.

system gains energy, the exchange is carried out. Otherwise, the exchange is performed with a probability $\exp(-\Delta E/kT)$, where ΔE is now the loss of energy ($\Delta E > 0$). The system evolves with successive jumps until it approaches the equilibrium configuration. We ensured that the system attained equilibrium by monitoring the island size distribution. The Monte Carlo results presented here were averaged over 100 samples.

In Figure 2, we compare, for $\varepsilon = 0$ and a defect density $D = 0.1$, the island size distribution given by the exact solution of equation (2) and Monte Carlo simulation outcomes. The results show that simulation and theory are in good agreement, and that defects change the slope of the distribution but not the exponential shape. As the coverage increases, it is expected that larger islands would form. However, defects act as an island-breaking mechanism, reducing the number of larger islands and increasing the number of the small ones. Figure 3 shows the effect of increasing the defect density keeping the coverage constant. Again, as expected, the slope increases with the defect density since islands are more likely to be split.

Figure 4 overleaf presents the island size distributions for interacting particles ($\varepsilon = 7kT$) and defects distributed at random. As can be easily seen, when interactions are present defects can change the exponential shape of the distribution (for $D = 0$) to a monomodal one. The stronger the energy involved, the smaller the density of defects needed to produce this change. The monomodal shape arises as a consequence of the competition between defects, which limit the island-growing process, and attractive interaction which favours particle aggregation. It is interesting to note that in the absence of surface defects, changing the shape of the distribution may be achieved by including more distant interactions of a repulsive character between particle island members (Mirabella and Aldao 2011; Tokar and Dreyssé 2003, 2007). These interactions can arise from the

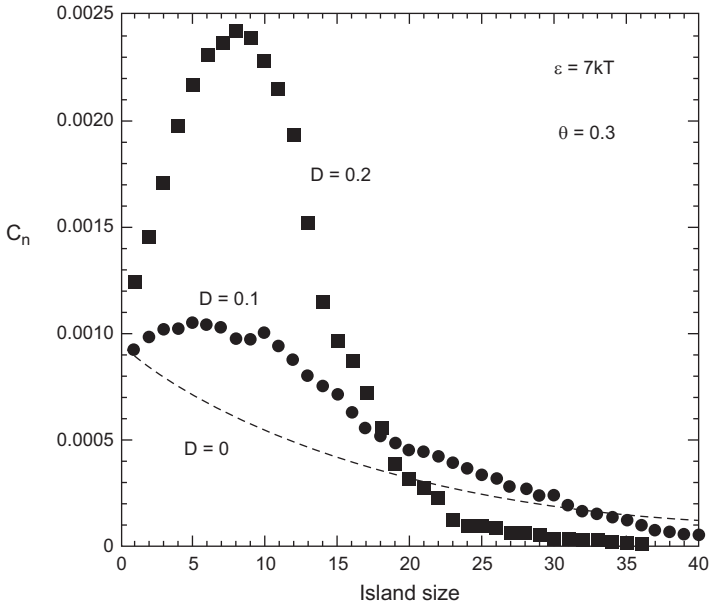

Figure 4. Island size distributions including interactions between first neighbours for $\theta = 0.3$, $\varepsilon = 7$ kT and $D = 0$, 0.1 and 0.2. Note that, without resorting to other mechanisms, defects can change the exponential distribution into a monomodal one.

strain resulting from the mismatch between the islands and the substrate. Indeed, hetero-epitaxial growth of strained structures offers the possibility of fabricating nano-scale islands with a very narrow size distribution. Here, we show that this type of interaction is not the only possible cause for having a monomodal island size distribution under equilibrium; this type of distribution can be due to the presence of defects.

A simple model for periodically distributed defects is developed below in order to gain an insight into the consequences of having defects on island distributions. To calculate the finite size confinement effects produced by defects, we proceed by re-writing equation (5) as follows:

$$\alpha c_n = \beta c_{n-1} c_1 \exp(\varepsilon/kT) \tag{11}$$

Equation (11) models the process of formation of an island of size n due to attaching a single particle to an island of size $n - 1$ and the reverse of this process, see equation (4). We restrict our analysis to the low-density limit where the probability of having more than one island between defects is negligible. The factor α on the left-hand side of equation (11) must take into account that not all particles detaching from islands find empty sites to form single-particle islands. On the other hand, the factor β on the right-hand side of equation (11) must take into account the fact that when a particle sticks to an island of size $n - 1$, an island of size n is not always formed (due to the presence of a defect). Here, we will consider that α equals 2 since there are two ends where the particle can be removed and, within the low-density limit, there are no restrictions to the formation of a single-particle island.

The factor β on the right-hand side of equation (11) is a correction that takes into account the presence of defects. This factor can be deduced by considering that, within a window of size ω (ω-sites), an island of size n − 1 has ω − n + 2 possible positions. In two of these positions, an island has only one side where a particle can attach because there is a defect on the other side. In the rest of the possible positions, there are two sites where a particle can attach to make an island of size n. Then, the average number of sites where a particle can be incorporated into an existing island of size n − 1 is:

$$\beta = 2\left(\frac{w - n + 1}{w - n + 2}\right) \tag{12}$$

Thus, the island size distribution for low coverages takes the following form:

$$c_n = \frac{w - n + 1}{w - n + 2} c_{n-1} c_1 \exp(\varepsilon/kT) \tag{13}$$

Figure 5(a) shows the results for the model, equation (13) and Monte Carlo simulation for three different interaction energies, inter-defect distance ω = 20 and θ = 0.3. It is interesting to note that, as the attractive interaction energy increases, the island size distribution changes from an exponential shape to one having a maximum. This is a consequence of the competition between confinement due to the inter-defect distance and the inter-particle attractive energy. The island size distributions shown in Figure 5(b) exhibit a maximum that shifts to the right as the attractive inter-particle interaction increases, since it favours the formation of large islands at the expense of small ones.

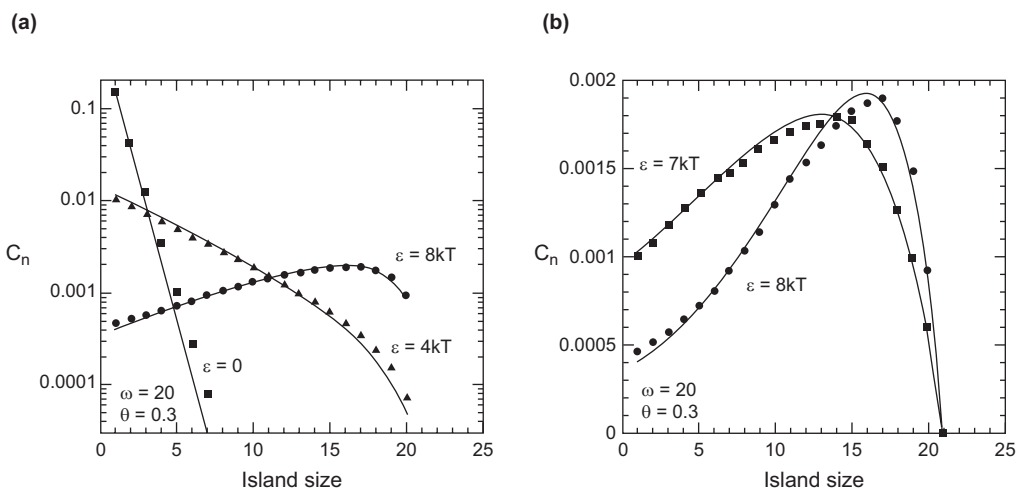

Figure 5. Island size distributions including interactions between first neighbours for θ = 0.3 and D = 0.05 with defects uniformly distributed, implying a constant distance between defects of ω = 20. Symbols correspond to Monte Carlo results while fitted lines correspond to equation (11). (a) ε = 0, 4 kT and 8 kT: as the attractive interaction energy increases, the island size distribution changes from an exponential shape to one that has a maximum. (b) ε = 7 kT and 8 kT. For the chosen parameters, distributions are monomodal and their maximum position depends on the particle interaction.

5. CONCLUSIONS

In this work, we have presented a Monte Carlo model that successfully reproduces the equilibrium island size distribution obtained for any coverage and nearest-neighbour interacting particles in 1D for a substrate with and without defects. It was found that, when defects were introduced into the model, a monomodal island size distribution, which was observed experimentally, could be obtained without resorting to more complicated mechanisms such as repulsive far-distant neighbour interactions due to surface stress. Using a simple model calculation for defects periodically arranged, we have shown how competition between defects and inter-particle interactions give raise to a monomodal distribution. Again, our findings reproduce the results obtained using Monte Carlo simulations.

ACKNOWLEDGMENTS

This work was supported by the ANPCyT (Agencia Nacional de Promoción Científica y Tecnológica, Argentina) and by the National Council for Scientific and Technical Research of Argentina (CONICET).

REFERENCES

Albao, M.A., Evans, M.M.R., Nogami, J., Zorn, D., Gordon, M.S. and Evans, J.W. (2005) *Phys. Rev. B* **72,** 035426.
Amar, J.G., Family, F. and Lam, P.M. (1994a) *Phys. Rev. B* **50,** 8781.
Amar, J.G., Popescu, M.N. and Family, F. (1994b) *Surf. Sci.* **491,** 239.
Barabási, A.L. (1999) *Mater. Sci. Eng. B* **67,** 23.
Chen, D. and Boland, J.J. (2004) *Phys. Rev. Lett.* **92,** 096103.
Daruka, I. and Barabási, A.L. (1997) *Phys. Rev. Lett.* **79,** 3708.
Gambardella, P., Brune, H., Kern, K. and Marchenko, V.I. (2006) *Phys. Rev. B* **73,** 245425.
Iguain, J.L., Mártin, H.O., Aldao, C.M., Gong, Y., Chey, S.J. and Weaver, J.H. (1998) *J. Vac. Sci. Technol. A* **16,** 3460.
Jensen, P., Barabási, A.L., Larralde, H., Havlin, S. and Stanley, H.E. (1994) *Phys. Rev. B* **50,** 15316.
Kamins, T.I., Carr, E.C., Williams, R.S. and Rosner, S.J. (1997) *J. Appl. Phys.* **81,** 211.
Medeiros-Ribeiro, G., Bratkovski, A.M., Kamins, T.I., Ohlberg, D.A.A. and Willimas, R.S. (1998) *Science* **279.** 353.
Meixner, M., Schöll, E., Shchukin, V.A. and Bimberg, D. (2001) *Phys. Rev. Lett.* **87,** 236101.
Mirabella, D.A. and Aldao, C.M. (2011) *J. Stat. Mech: Theory Exp*. P03011.
Owen, J.H.G., Miki, K. and Bowler, D.R. (2006) *J. Mater. Sci.* **41,** 4568.
Priester, C. and Lannoo, M. (1995) *Phys. Rev. Lett.* **75,** 93.
Ross, F.M., Tersoff, J. and Tromp, R.M. (1998) *Phys. Rev. Lett.* **80,** 984.
Tokar, V.I. and Dreyssé, H. (2003) *Phys. Rev. E* **68,** 011601.
Tokar, V.I. and Dreyssé, H. (2007*) Phys. Rev. B* **76,** 073402.
Vavro, J. (2001) *Phys. Rev. E* **63,** 057104.
Yilmaz, M.B. and Zimmermann, F.M. (2005) *Phys. Rev. E* **71,** 026127.