

# Coalescence and impingement between islands in thin film growth: Behavior of the island density kinetics

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Coalescence and impingement, which in the time domain give rise to completely different kinetics for the density of islands, are shown to lead to common kinetics in the domain of the fraction of covered surface in the case of thin-film growth after simultaneous nucleation. This result allows one to treat the more involved intermediate case (partial coalescence) in a rather straightforward way. On this basis experimental data taken from the literature are discussed and reanalyzed in order to evaluate the saturation density of the nuclei.

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## I. INTRODUCTION

The collision among islands is certainly one of the main questions that a theoretical model must face in order to describe the island density kinetics in film growth. After collision two limiting cases can be distinguished namely, *coalescence* and the *impingement*. In the former case redistribution of matter among islands occurs under conservation of both mass and island shape and, as far as the three-dimensional (3D) island case is concerned, by a reduction of surface coverage. In the latter case no redistribution of matter occurs after collision among islands. The growth of a droplet pattern, which condenses onto a substrate is a paradigmatic case of coalescence. Briscoe and Galvin<sup>1</sup> have studied this case rather thoroughly. Their analysis leads to a system of first-order differential equations that links the fraction of covered substrate surface,  $S$ , the mean diameter of droplets  $D_2$ , and the number of droplets (in general, islands)  $N$ . Moreover, they rederived the empirical equation that was firstly proposed by Vincent.<sup>2</sup> As far as the second case is concerned, the kinetic of number of islands was recently investigated.<sup>3</sup> Besides evaluating the exact formal solution and proposing a rather good approximation of it, the definite behavior was determined through a Monte Carlo simulation.<sup>4</sup> Moreover, from the knowledge of  $N(S)$  and the lifetime of the monomer, the capture factor was also evaluated.<sup>5</sup> The theoretical predictions have been successively confirmed experimentally by studying the growth of diamond onto a silicon substrate.<sup>6</sup> This system can be rightfully considered the paradigmatic case for growth ruled by impingement.

The majority of thin-film growths cannot be assigned sharply to one of these two aforementioned categories, rather the rule is an intermediate regime that is often referred to as incomplete or partial coalescence. In this respect, it is worth quoting the recent data regarding the deposition of Au on TiO<sub>2</sub>(110) and of Ag, Co, and Fe on Si/CaF<sub>2</sub>.<sup>7,8</sup> It goes without saying that to develop an analytical model for such a kinetics is a formidable task. As a matter of fact this issue has been tackled by Yu *et al.* through a computer simulation.<sup>9</sup>

Before going through the core of the work, a remark concerning the nomenclature is in order. In the following we will distinguish between cluster and island. The former is an aggregate of atoms related to a single nucleation event. The latter is any isolated object that is in general made up of connected clusters. In case of film growth governed by the impingement mechanism, clusters retain their individuality in the island after collision.

One of the aims of this work is to study the effect of impingement and of coalescence mechanisms on the island density kinetics. To this end computer simulations will be presented for film growth driven by either coalescence or impingement mechanisms in case of simultaneous nucleation of the islands and for several shapes of the clusters. Both 2D and 3D clusters are considered. In addition, one has to keep mind of the fact that the two mechanisms, coalescence and impingement, lead to very different behavior both for  $S(t)$  and  $N(t)$  kinetics, as shown in Fig. 1. In particular, the coalescence kinetics has been computed according to Vincent's model,<sup>1,2</sup> while the impingement kinetics was computed through the Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory.<sup>10,11</sup> However, by plotting  $N$  vs  $S$  it happens that the

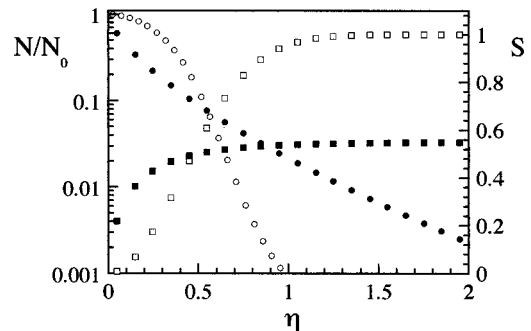


FIG. 1.  $N(\eta)$  (circles) and  $S(\eta)$  (squares) kinetics for film growth ruled by coalescence (full symbols) and impingement (open symbols) mechanisms where  $\eta = h\sqrt{N_0}$ ,  $h$  being the film thickness. In case of film growth driven by impingement, the kinetics have been computed using the JMAK model (Refs. 3–5) with cluster diameter given by  $D = 2Ft/\rho = 2h$ ,  $F$  and  $\rho$  being, respectively, the flux and the overlayer density.

two behaviors are not so different as in the time regime, as shown in this work. Moreover, the typical experimental error for island density number ranges from 10%, at  $S \approx 0.1$ , up to 60%, at  $S \approx 0.6$  at least for the data set considered here. This allows one to describe both behaviors by the same function and the experimental data can be analyzed in a very easy fashion without introducing any ad hoc hypothesis for the redistribution mechanism of matter.

## II. A MEAN FIELD EQUATION FOR COALESCENCE KINETICS

To begin with, we consider a mean-field approach to the kinetics of island coalescence under the following assumptions: (i) islands are randomly distributed throughout the surface, and (ii) only binary collisions are taken into account,<sup>12</sup> thus the following rate equation holds:

$$\frac{dN}{dt} = -2N^2 \frac{d(\pi D^2/4)}{dt}, \quad (1)$$

where  $D^2 = (\sum_i D_i^2/N)$  is the mean-square diameter. In Eq. (1) the term  $d(\pi D^2/4)/dt$  plays the role of rate coefficient. Since

$$S = \frac{N\pi D^2}{4} \quad (2)$$

Eq. (1) becomes

$$\frac{dN}{N} = -\frac{d(2S)}{1-2S} \quad (3)$$

and the solution reads

$$\frac{N}{N_0} = 1 - 2S. \quad (4)$$

For small  $S$  the Stowell-Hutchinson approximation,<sup>13</sup>  $dN \cong -2NdS$ , is recovered from Eq. (3). In the case of coalescence the shape of the island is known at any time of the growth and Eq. (4) can be easily exploited to evaluate the  $S(t)$  [and consequently the  $N(t)$ ] kinetics. Equation (4) holds for both 2D and 3D island growths. However, while for 2D its reliability is confined to the initial stage of the kinetics ( $S \approx 0.3$ ), as we will show shortly, in case of 3D pure coalescence Eq. (4) results to be valid, in fact, in the whole kinetics. In order to substantiate the latter point, we employ Eq. (4) for evaluating the  $S$  kinetics.

For hemispherical islands the film thickness  $h$  is given by

$$h = \frac{Ft}{\rho} = \frac{\pi N D_3^3}{12}, \quad (5)$$

where  $D_k = (\sum_i D_i^k/N)^{1/k}$  is the mean diameter in the  $k$  basis,  $F$  is the flux, and  $\rho$  is the overlayer density.<sup>1</sup> Briscoe and Galvin showed that, for relatively narrow distribution of the island radius, the ratio between the mean radius on a volume and on an areal basis is given by

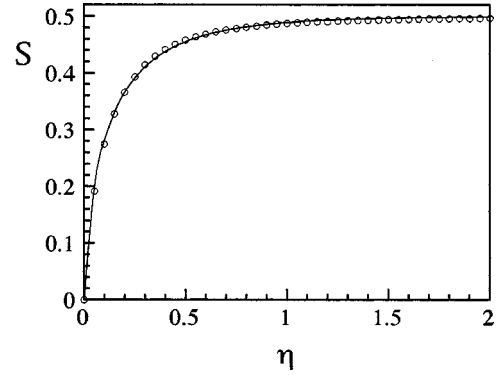


FIG. 2. Kinetics of the covered surface,  $S(\eta)$ , for film growth by coalescence mechanism. The analytical computation obtained through the mean-field theory for  $m=1.07$  [Eq. (7), open symbols] reproduces Vincent's solution (Refs. 1 and 2) and is displayed as a continuous line.

$$\frac{D_3}{D_2} = m, \quad (6)$$

with  $m$  in the range 1.00–1.05.<sup>1</sup> By making use of the expressions (2), (4), and (6), Eq. (5) is eventually rewritten according to

$$\xi(h)S^2 + 2S - 1 = 0, \quad (7)$$

where  $\xi(h) = 4m^6/9\pi N_0 h^2$  and  $S(h \rightarrow \infty) = \frac{1}{2}$ . The  $S(h)$  kinetics is therefore given by the real root of Eq. (7) whose evaluation is obtained analytically. The result is displayed in Fig. 2, as a function of the dimensionless quantity  $\eta = h\sqrt{N_0}$ , and compared with Vincent's equation for  $P_0 = \frac{1}{2}$ .<sup>14</sup> Equation (7) perfectly reproduces Vincent's kinetics for  $m = 1.07$ , a value in excellent agreement with Ref. 1.

As far as the impingement mechanism is concerned, the island density as a function of  $S$  has been determined in case of simultaneously nucleated square clusters through a computer simulation<sup>4</sup> and by a mean-field theory.<sup>15</sup> In particular, the analytical computation is found to be in excellent agreement with the numerical kinetics, up to  $S=0.7$ , confirming the reliability of the mean-field approach even for this mechanism.

## III. COMPUTER SIMULATIONS

The effect of coalescence and impingement on the island density kinetics can be thoroughly investigated through computer simulations. We performed numerical computations for both 2D and 3D islands for several shapes of the clusters and in the case of simultaneous nucleation. For the coalescence kinetics the computer algorithm is similar to that employed in Ref. 4 for evaluating the island density in film growth ruled by impingement. However, at variance with the impingement case, when two or more islands collide they merge, instantaneously, into a new island located at their center of mass under conservation of both mass and shape. It goes without saying that for 2D islands a coalescence event does not lead to any change in the value of the substrate area that is covered by islands. Conversely, coalescence in three

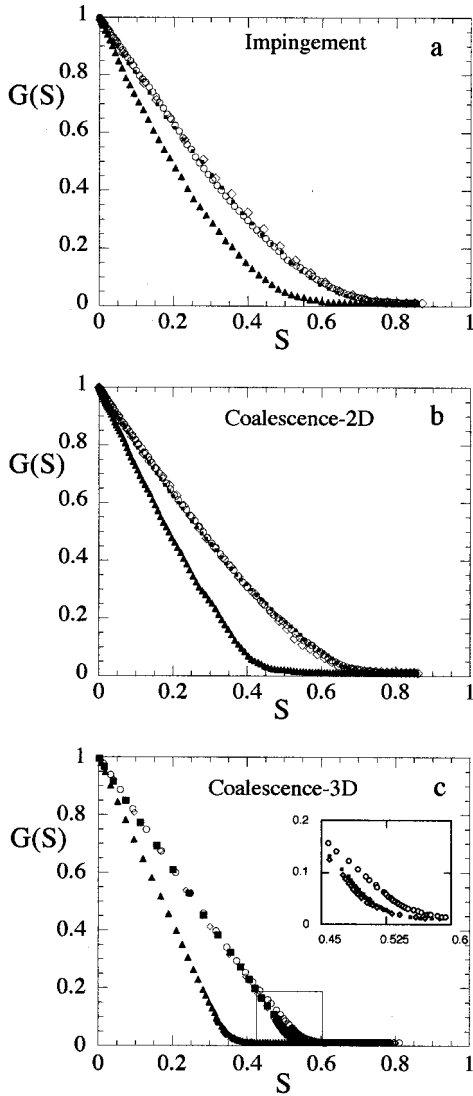


FIG. 3. The island density behavior for film growth ruled by impingement is displayed in panel (a). Panels (b) and (c) show the  $G(S)$  vs  $S$  kinetics in case of growth governed by coalescence of 2D and 3D islands, respectively. In the plots triangles, squares, diamonds, and circles refer to the 2D projection of the cluster, on the substrate surface, which is a triangle, a square, a hexagon, and a circle.

dimensions is accompanied by a reduction of the surface coverage and, as a consequence, the jamming point is reached at  $S < 1$ .

Computer simulation of 3D island growth ruled by coalescence has been performed for several shapes of the islands, namely (i) hemisphere, (ii) cube, (iii) equilateral triangular pyramid, and (iv) a prism whose base is a regular hexagon with side equal to the prism height. With regard to the impingement mechanism, simulations were carried out for clusters whose 2D projection, on the substrate surface, is a circle, a square, an equilateral triangle, and a hexagon. Apparently for this collision mode island density behavior, in the  $S$  domain, is the same for both 2D- and 3D-island growths provided the growth law of the 2D projection of the cluster does not change after collision.

The results of the computer simulations are shown in Fig. 3 for growth modes governed by impingement and coalescence mechanisms. Specifically, in panels (a)–(c) the functions  $G(S) \equiv N(S)/N_0$  versus  $S$  have been reported for the impingement mechanism [panel (a)] and in case of 2D and 3D island coalescence, respectively [panels (b) and (c)]. As it appears, in the case of circular, square, and hexagonal 2D projection of the cluster, the island density behavior exhibits no appreciable differences, provided the growth morphology is the same. Conversely, in case of triangular symmetry the kinetics is quite different with respect to the other geometries.

To study the effect of the growth morphology on the behavior of the island density kinetics, the results of Fig. 3 have been collected, as displayed in Figs. 4(a)–4(d), according to the geometry of the cluster. This comparison clearly shows that for the geometries considered here and in case of 2D-island growth, the island density kinetics is independent of the collision mechanism. On the basis of Fig. 4 we also infer that even the intermediate cases, i.e., partial coalescence, should follow the same kinetics. It is worth noting that since the coalescence of two 2D islands is not accompanied by a decrease of surface coverage, the jamming point is actually attained at  $S = 1$ .

As far as the 3D-island density kinetics is concerned, Fig. 4 shows that it differs from the impingement one only at high coverages. Specifically, we deduce that, for a given shape of cluster, film growths driven by either coalescence or impingement, in the  $S$  domain, are described by the same  $G(S)$  function provided  $S < \bar{S}$ , with  $\bar{S} \cong 0.3$  for triangle and  $\bar{S} \cong 0.4$  for the other geometries. It is

$$G(S) = \frac{N(S)}{N_0} \cong 1 - aS, \quad (8)$$

where  $a$  is a constant. Moreover, we speculate that even the intermediate cases, i.e., partial coalescence, follow the same kinetics. We find an  $a$  value that is about 1.85 for all the geometries with an exception for the triangular shape for which an  $a$  value, as large as 2.77, is obtained. Moreover the deviation of Eq. (4) from the simulations, in the 2D case, could be due to the failure of the binary collision hypothesis in the high-coverage regime.

It is evident from our simulations (Fig. 3) that the  $G(S)$  kinetics is, in fact, independent of cluster shape, apart from the triangle. Consequently, very close percolation thresholds for the impingement mechanism are also expected. These values, which are reported in Table I, confirm what we stated

TABLE I. 2D percolation threshold,  $S_c$ , for various geometries. The  $S_c$  values (squares and circles) are in good agreement with those of Ref. 16. In addition, the percolation onset for the hexagonal symmetry does not deviate, significantly, from the  $S_c$  value for circular clusters. The error is the standard deviation of the mean.

|              | Triangle          | Square          | Hexagon         | Circle            |
|--------------|-------------------|-----------------|-----------------|-------------------|
| Present work | $0.476 \pm 0.008$ | $0.64 \pm 0.01$ | $0.68 \pm 0.01$ | $0.665 \pm 0.010$ |
| Reference 13 |                   | 0.66            |                 | 0.68              |

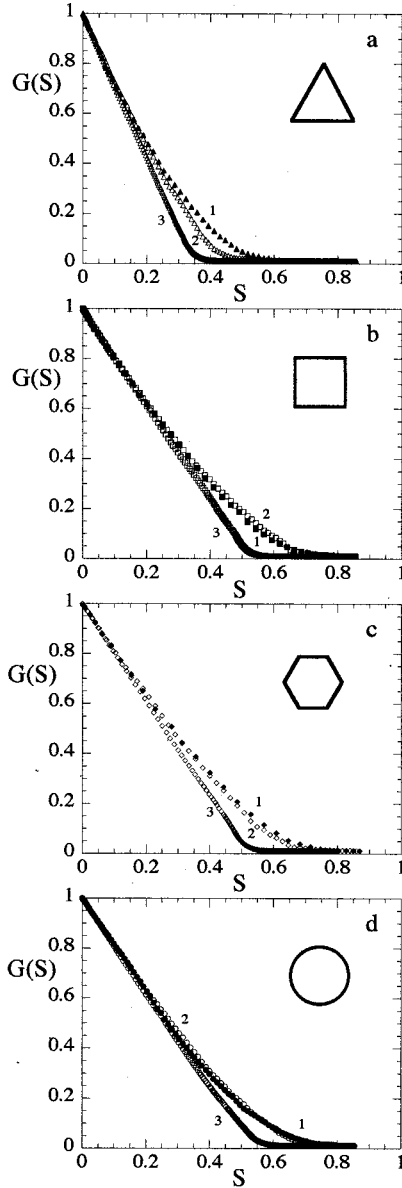


FIG. 4. Behavior of the island density kinetics for a given cluster geometry in case of film growth governed by coalescence and impingement. Full symbols refer to the impingement case (curve 1) while open symbols refer to the 2D (curve 2) and 3D (curve 3) island coalescence, respectively. (a) triangle and pyramid; (b) square and cube; (c) hexagon and prism; (d) circle and hemisphere. We remember that with regard to the impingement mechanism, one always refers to the geometry of the 2D projection of the clusters.

and are compared, for the square and circle, to those ones previously published in the review by Isichenko.<sup>16</sup>

#### IV. APPLICATION TO EXPERIMENTAL DATA

In order to substantiate our conjecture we analyze in this spirit some recent experimental data available from the literature: the growth of Au on TiO<sub>2</sub> by Zhang *et al.*<sup>7</sup> of Fe, Co, and Ag on CaF<sub>2</sub> by Heim *et al.*,<sup>8</sup> and Ag on GaAs (001) 2 × 4 by Fanfoni *et al.*<sup>17</sup> However, before proceeding further,

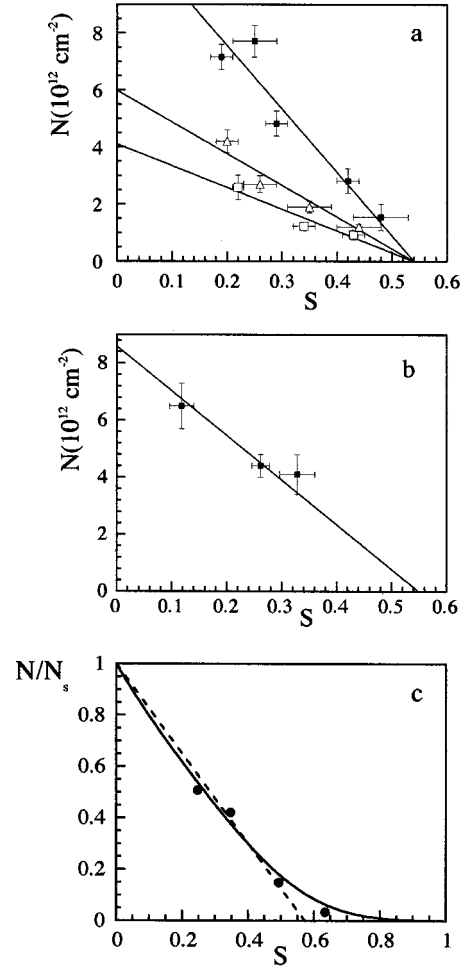


FIG. 5. Island densities as a function of the fraction of the covered surface. (a) Experimental data from Ref. 8 regarding the growth of Fe (full symbol), Co (open triangles), and Ag (open squares) on Si/CaF<sub>2</sub> substrate. (b) Data from Ref. 17 on the growth of Ag on GaAs(001)2 × 4. Solid lines are best fits of Eq. (8) to the data. (c) Data from Ref. 7 on the Au/TiO<sub>2</sub> system (symbols). The solid line is the  $G(S)$  kinetics for the impingement case. Saturation densities obtained by the fits are (a)  $N_n(\text{Fe}) = (11.8 \pm 0.8) \times 10^{12} \text{ cm}^{-2}$ ,  $N_n(\text{Co}) = (5.9 \pm 0.4) \times 10^{12} \text{ cm}^{-2}$ , and  $N_n(\text{Ag}) = (4.1 \pm 0.3) \times 10^{12} \text{ cm}^{-2}$ ; (b)  $N_n(\text{Ag}) = (8.5 \pm 0.5) \times 10^{12} \text{ cm}^{-2}$ ; (c)  $N_n(\text{Au}) = 2.5 \times 10^{12} \text{ cm}^{-2}$ .

as the nucleation is in general not simultaneous, an outline of our approach<sup>4</sup> to treat this case is necessary.

In the framework of the mean-field approach the number of islands per unit surface can be written as

$$N(S) = \nu(S)G(S), \quad (9)$$

where  $G(S)$  is the function that takes into account the reduction of the island density due to collision and  $\nu(S)$  is the number of nucleation events up to  $S$ . Beyond the nucleation stage, say for  $S > S_n$ , clearly

$$N(S) \cong \nu(S_n)G(S), \quad (10)$$

where  $S_n$  can be identified with the saturation point of the nucleation kinetics.<sup>12</sup> In the following  $N_n = \nu(S_n)$ .

In Fig. 5(a) the  $N(S)$  experimental data of Ref. 8 are shown. At this point it is the case to resume how, in Refs. 7 and 8, the authors analyzed the data. The validity of the Vincent's formula is assumed *a priori* and through it the  $N_0$  parameter is determined. Afterwards, the plot of the coverage as a function of  $N/N_0$  is used to check the consistency of the initial assumption. In Ref. 8 the authors find that Fe and Co growths are not described by Vincent's model and conclude that these two metals, at variance with Ag, do not grow in coalescence regime.

By reason of the large error affecting the experimental data, which is comparable to the difference between the impingement and the 3D coalescence modes, we propose to describe the experimental data by using the same  $G(S) \cong 1 - aS$  kinetics (for  $S < 0.5$ ) irrespective of the regime of growth. The  $a$  parameter is chosen in such a way that the straight line is the average between the coalescence and impingement curves. Moreover, apart from triangular symmetry, we found  $a = 1.85$ . It is interesting to note that our estimate of the only fitting parameter,  $N_n$ , coincides, within the error, with that obtained from Fig. 8 of Ref. 8 (i.e.,  $\ln N$  vs  $h^{2/3}$  plot) only for the case of Ag, that is, for the only metal that fulfills Vincent's model. We found  $N_n = (4.1 \pm 0.3) \times 10^{12} \text{ cm}^{-2}$ , whereas Heim *et al.* found  $N_n = (4.7 \pm 0.5) \times 10^{12} \text{ cm}^{-2}$ .<sup>18</sup> Also the islands of Ag on GaAs (001)  $2 \times 4$  exhibits two regimes: after an initial period in which their base is about a square and they do not show a clear cut 3D shape, they undergo a shape transition toward a rectangular base and a definite 3D shape.<sup>17</sup> The behavior of  $N(S)$  is reported in Fig. 5(b) and we get  $N_n = 8.5 \times 10^{12} \text{ cm}^{-2}$ .

The last set of data we are going to discuss, which is from

Zhang *et al.*, regards the growth of Au on  $\text{TiO}_2$ .<sup>7</sup> Analyzing the experimental island density by assuming film growth driven by coalescence, the authors showed that Vincent's equation does not describe the data. This argument is confirmed by high-resolution scanning electron microscopy measurements of the morphology of the Au islands. Specifically, the Au islands evolve from the initially dropletlike islands ( $S < 0.3$ , the first regime of growth), to wormlike islands at  $S > 0.3$  (second regime). During film growth a transition occurs in the mechanism of matter redistribution between islands. As the redistribution of matter is inhibited in the second regime, the Zhang *et al.* results ought to be well described by the  $G(S)$  function of growth governed by impingement.<sup>6</sup> In fact, the kinetics of the island density extends beyond  $S = 0.65$ , namely, beyond the "jamming limit" ( $S = 0.55$ ), which characterizes the coalescence kinetics. The result of our analysis is depicted in Fig. 5(c) for the  $N/N_n$  kinetics and indicates a very good agreement between the theory and the experiment. Also the  $N_n$  density has been determined by the best fit of Eq. (8) to the first three experimental points. The value of  $N_n$  is found to be approximately twice the figure obtained by processing the data according to a full coalescence mechanism.<sup>7</sup>

In conclusion we have shown that, once studied in the  $S$  domain, the kinetics of the island density is nearly independent of the mechanism of matter redistribution among islands. This universal behavior may be profitably exploited for estimating the nucleation density at saturation by means of experiments performed in the regime of the high surface coverages ( $S \geq 0.2$ ) where island imaging does not require atomic resolution.

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<sup>14</sup>In case of hemispherical islands Vincent's equation for the  $S$  kinetics reads  $S(\eta) = P_0(1 - e^{-(18\pi)^{1/3}\eta^{2/3}})$ , where  $0.5 < P_0 < 0.6$  and  $\eta = h\sqrt{N_0}$ ,  $h$  being the film thickness. Moreover, the  $N/N_0$  ratio is found to scale as  $N/N_0 = 1 - (1/P_0)S$  (Ref. 2).

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<sup>18</sup>In film growth driven by coalescence the island density, as a function of film thickness, reads  $N(h) = N_0 e^{-Ah^{2/3}}$ ,  $A$  being a constant. This equation holds for simultaneous nucleation. Nevertheless, the conclusion reached in Ref. 3 applies also to this case provided  $N_0$  is the whole number of nucleation events,  $N_n$ .