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Closed-form theory of nuclei separation on highly anisotropic surfaces

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ABSTRACT

During deposition on surfaces of highly anisotropic diffusion, nucleation behaves as it would on a one-dimensional substrate, or effectively deposition in two-dimensions (2D). This Article reports a close-form theory for nuclei separation during physical vapor deposition in 2D. In comparison and contrast, this closed-form theory agrees with existing theories in scaling, but gives the coefficient that was previously unknown. Further, this theory shows that the nuclei separation in 2D is an order-of-magnitude larger than in three dimensions. The insights from such comparison and contrast are critical in analyzing nucleation on surfaces of various anisotropy.

1. Introduction

Nucleation of atomic clusters on a solid substrate is generic in many surface processes, such as physical vapor deposition (PVD). As shown in Fig. 1, the area density of nuclei first increases with deposition time or coverage, reaches a maximum, and then decreases as some nuclei start to merge. Under glancing angle PVD on a non-wetting substrate, the merge of nuclei can be avoided and nanorods develop. As a result, the nuclei separation at the maximum area density also defines the separation of nanorods, and is called the critical separation. This quantity of critical separation has been exhaustively investigated, for example references [1,2]. However, this line of thinking has not led to an analytical or closed-form theory of the critical separation.

An analytical or closed-form theory of the critical nuclei separation becomes possible, as we think and formulate in a different phase space; shown in Fig. 1. In the new phase space, one variable is the separation of existing nuclei on a substrate. As the separation increases, the other variable – the nucleation probability of forming additional clusters on the substrate – goes from 0 to 1. The critical separation is the separation at which the nucleation probability sharply transitions from 0 to 1. Following this logic, we have obtained a closed-form theory of the critical separation in three dimensions (3D) [3], and further used it to guide the experimental realization of the smallest and well-separated nanorods from PVD [4].

It might appear illogical to develop a closed-form theory in 2D, when it is already available in 3D. However, that appearance is incorrect here. There are two good reasons for this investigation in 2D. First, surface diffusion can be highly anisotropic on some crystalline surfaces such as on the 2×1-dimer-reconstructed Si {001} surfaces [5]. In this case, nucleation is dominated by atomic diffusion along one dimension of the surface and atomic deposition along the other dimension – that is, the theory in 2D applies. Second, 2D atomistic simulations are still useful because of their reach to larger length and longer time scales than 3D atomistic simulations. To properly appreciate the simulation results, it is important to be able to analytically comprehend the order-of-magnitude differences between physical quantities in 2D and those in 3D.

In this Article, we first derive the closed-form theory of the critical separation of nuclei in 2D. Then we use lattice Kinetic Monte Carlo (KMC) simulations to verify the theory. By comparison and contrast of the two analytical theories in 2D and 3D, we show that under typical PVD conditions the average separation of nuclei in 2D is an order of magnitude larger than in 3D.

2. Closed-form theory

In deriving the theory, we consider a representative nucleation space $x \in \left[-\frac{L-D}{2}, \frac{L-D}{2}\right]$ as shown in Fig. 2. Following the same approach as in our previous report [3], we first derive the analytical expression of adatom concentration on a flat substrate. Based on the concentration, we then determine the nucleation probability, and therefore the critical separation. Due to the different time scales of deposition and diffusion, the adatom concentration $n(x)$

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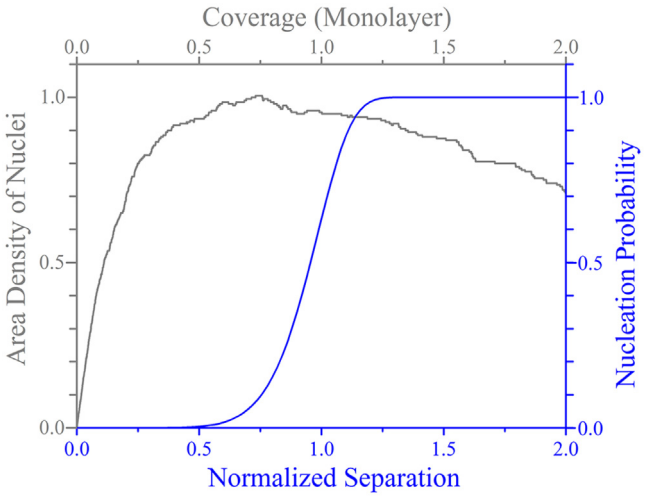

Fig. 1. Schematic of area density of nuclei, which is normalized so the maximum density is 1, as a function of coverage; and nucleation probability as a function of separation of nuclei, which is normalized so the critical separation is 1.

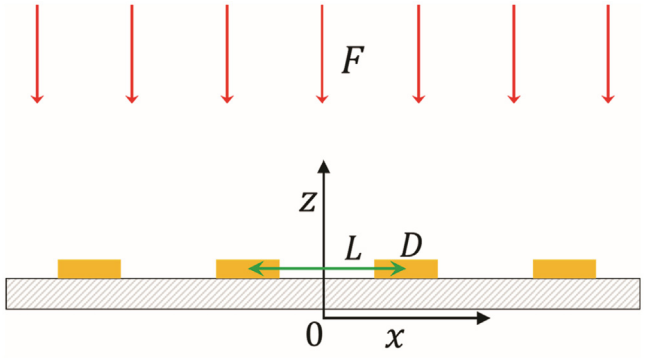

Fig. 2. Schematic of deposition in 2D, with existing nuclei of diameter D and separation L, and deposition rate F.

reaches a quasi-steady state between two deposition events [6,7]. Therefore, the governing diffusion equation is:

$$\frac{\nu}{2}\nabla^2 n(x) + F = 0 \tag{1}$$

where ν is the adatom diffusion jump rate. The adatom concentration $n(x)$ is fractional and the length x is in unit of the nearest neighbor distance (lattice unit). The deposition rate F is in unit of monolayer per second (ML/s). The first boundary condition is that the adatom concentration is zero near a nucleus, and the second boundary condition is that there is no net flux at $x=0$ due to symmetry. The adatom concentration under these boundary conditions is:

$$n(x) = \frac{F}{\nu}\left[\left(\frac{L-D}{2}\right)^2 - x^2\right] \tag{2}$$

As previously shown [8], the conventional nucleation theory does not apply here because only one adatom exists on the surface most of the time. Instead, the nucleation probability per unit length follows the lone-adatom-model (LAM) and is [9]:

$$p = \frac{\tau}{\Delta t} \tag{3}$$

Here, the residence time per unit length τ is the ratio between the average adatom concentration and the deposition rate F, and the time interval between two consecutive deposition events Δt is $1/[F(L-D)]$. The total nucleation rate is:

$$w = (L-D)pF = \frac{F^2(L-D)^4}{6\nu} \tag{4}$$

The total nucleation probability P is governed by $dP/dt = w(1-P)$. Under the condition of no extra energy barrier for the interlayer adatom transport, we have $D = FLt$. During the deposition of one ML, the space for nucleation goes from 0 to L, and the nucleation probability is:

$$P = 1 - e^{-\int_0^{\frac{1}{F}} w dt} = 1 - e^{-\frac{F}{30\nu}L^4} = 1 - e^{-\left(\frac{L}{L_0}\right)^4} \text{ with } L_0 = \left(\frac{30\nu}{F}\right)^{\frac{1}{4}} \tag{5}$$

The constant in the exponent, L_0, has been referred to as the critical length; for example, critical separation [3] and critical island size [9]. However, the measured critical separation may be slightly different from L_0. In the following, we will show that the difference is a factor of 0.91. Based on the nucleation probability in Eq. (5), the nucleation probability density in L space is:

$$\frac{dP}{dL} = \frac{4L^3}{L_0^4} e^{-\left(\frac{L}{L_0}\right)^4} \tag{6}$$

Over a large ensemble, the measured value of the critical separation is:

$$L_s = \int_0^{+\infty} L\frac{dP}{dL}dL = \Gamma\left(\frac{5}{4}\right)L_0 \approx 0.91\left(\frac{30\nu}{F}\right)^{\frac{1}{4}} \tag{7}$$

where $\Gamma(x) = \int_0^{+\infty} e^{-t}t^{x-1}dt$ is the Gamma function. The critical separation so defined is the measured value and can be compared directly with computer simulation or experimental results. It differs from the constant L_0 by a factor of 0.91; in 3D, this factor becomes 0.93 or $\Gamma\left(\frac{7}{6}\right)$. For consistency, we will from now on always refer the critical separation to mean the measured value as in Eq. (7), instead of the constant in the exponent as in Eq. (5).

We note that the concept of nucleation probability as a function of length has been employed for the case of nucleation on an island. However, the concept had not been employed for the case of separation between nuclei, before our recent report [3]. In comparison with previous reports [8,10,11], Eq. (7) gives the same scaling $\frac{\nu}{F}^{\frac{1}{4}}$. In contrast, Eq. (7) also gives the coefficient $0.91(30)^{\frac{1}{4}}$, which was previously unknown. The validity of Eq. (7), particularly the coefficient, will be verified using lattice KMC simulations.

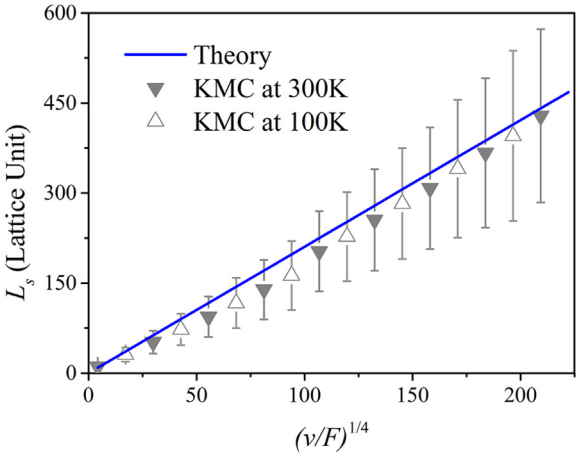

Fig. 3. Comparison of the closed-form theory and KMC simulation results, with the error bar representing the standard deviation.