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A theory of growing crystalline nanorods – Mode I

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ABSTRACT

Nanorods grow in two possible modes during physical vapor deposition (PVD). In mode I, monolayer surface steps dictate the diameter of nanorods. In mode II, multiple-layer surface steps dictate the diameter, which is the smallest possible under physical vapor deposition [5,10]. This paper reports closed-form theories of terrace lengths and nanorod diameter during the growth in mode I, as a function of deposition conditions. The accompanying lattice kinetic Monte Carlo simulations verify these theories. This study reveals that (1) quasi-steady growth exists for each set of nanorod growth conditions, and (2) the characteristic length scales, including terrace lengths and nanorod diameter at the quasi-steady state, depend on the deposition conditions – deposition rate F, substrate temperature T, and incidence angle θ – only as a function of $l_{2D}/\tan\theta$, with $l_{2D} = 2\left(\frac{v2D}{F\cos\theta}\right)^{\frac{1}{3}}$ as a diffusion-limited length scale and v_{2D} as the atomic diffusion jump rate over monolayer surface steps.

1. Introduction

The growth of crystalline nanorods through physical vapor deposition (PVD) proceeds in two possible modes. In comparison, both modes rely on the incidence angle being glancing or oblique during the experiments [1–4]. In contrast, the growth of mode I relies on monolayer surface steps and that of mode II relies on multiple-layer surface steps to limit the surface diffusion or mass transport [5]; and typically the growth of mode I takes place on a wetting substrate, and that of mode II takes place on a non-wetting substrate [6].

The growth of mode II leads to the smallest diameter of nanorods, due to the large three-dimensional Ehrlich-Schwoebel (3D ES) diffusion barrier over multiple-layer surface steps [7–9]. Driven by the stronger desire of growing smaller nanorods, the theory of nanorod diameter for growth of mode II has been formulated before that of mode I, verified by atomistic simulations, and validated by PVD experiments [5,10]. This theory, coupled with the theory of nanorod separation [11], has enabled the design of not only small but also well-separated nanorods, and their experimental realization [5]. The availability of small and well-separated metallic nanorods has in turn resulted in the technology of metallic glue [12,13].

The growth of mode I leads to a larger diameter of nanorods than that of mode II does, because of the smaller two-dimensional Ehrlich-Schwoebel (2D ES) diffusion barrier over monolay-layer surface steps [14,15]. However, this growth mode bridges with that of thin films, and is therefore scientifically interesting [16,17]. For thin films, the wedding cake model [18–20] incorporates the effects of 2D ES barriers and builds on the BCF theory [21], but excludes the effects of non-zero incidence angle. Incorporating the effects of non-zero incidence angle, a recent theory shows that the growth of thin film transitions to the nanorod growth of mode I at a critical coverage and above a critical incidence angle [22]. Beyond this transition point, an important characteristic length scale is the diameter of nanorods, and it is the primary focus of this invesitgation.

This paper reports a closed-form theory of the nanorod diameter, in terms of deposition conditions – substrate temperature (or diffusion jump rate), deposition rate, and incidence angle of deposition flux – as well as nanorod separation, which depends on deposition conditions and substrate patterns. Further, this paper also reports closed-form theories of terrace lengths, the sum of which defines the nanorod diameter.

2. Theory

We first conceptually describe in Section 2.1 the framework of theoretical formulations, in terms of (1) characteristic length scales of interest, (2) quasi-steady state condition, and (3) number of coupled equations vs number of physical unknowns. In Section 2.2, we present theoretical formulations for quasi-steady state growth and numerical results to gain insights of terrace lengths as a function of time. In Section 2.3, we take into account the gained insights to derive approximate and closed-form theories, and numerically show the validity of the approximation. In Section 2.4, we use lattice kinetic Monte Carlo (KMC) simulations to verify the closed-form theories.

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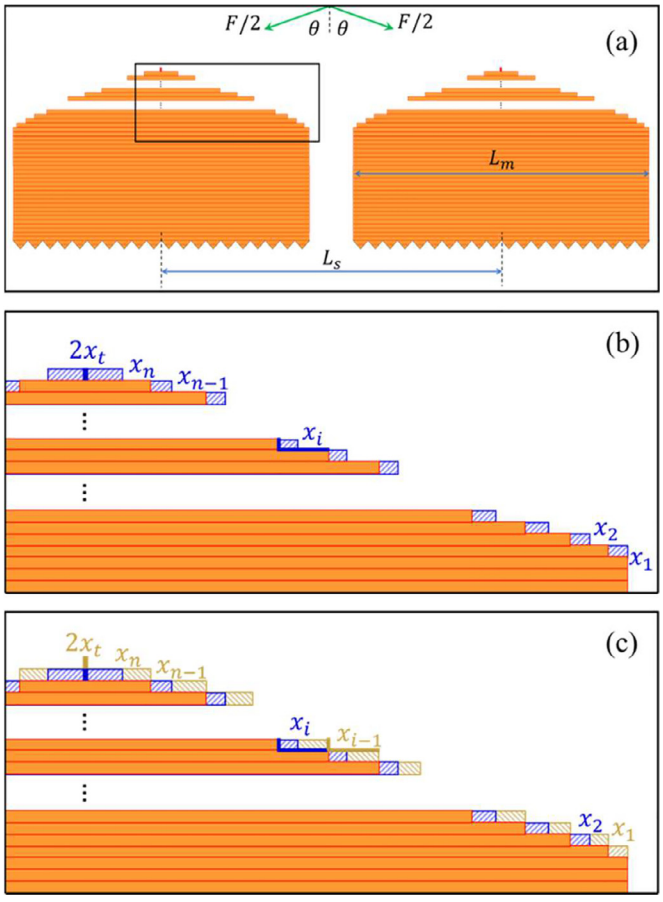

Fig. 1. (a) Schematic of nanorod morphologies at quasi-steady state, (b) surface morphology from time zero shown as solid to τ_0 with newly grown region shown as meshed blue, and (c) surface morphology from time τ_0 to τ with newly grown region shown as meshed tan. The ith step and the ith terrace of length x_i are marked by solid lines, to illustrate their relative positions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The KMC simulations are for the epitaxial growth of a prototype Cu [5,22,23]. As a brief recap of the simulations, atoms with one coordination has a diffusion hopping rate of $v_s = v_0 e^{-E_S/kT}$ on flat surfaces, $v_{2D} = v_0 e^{-E_{2D}/kT}$ over monolayer surface steps, and $v_{3D} = v_0 e^{-E_{3D}/kT}$ over multiple-layer surface steps. Here, v_0 is 5×10^{11} /s, E_s is 0.06 eV, E_{2D} is 0.16 eV and, E_{3D} is 0.40 eV [7,9] and kT is the Boltzmann factor. As discussed in Ref. [24], in order to have a comparable length scale of surface islands as in three dimensions under typical room temperature of 300 K and typical deposition rate of 1 nm/s, the substrate temperature in two-dimensional simulations needs to be choosen around 100 K.

2.1. Conceptual framework

Based on experimental observations [1–4], and as shown later by KMC simulations, the mode I growth of nanorods will reach a quasi-steady state. Fig. 1(a) illustrates the top section of nanorods at quasi-steady state – a wedding cake like top surface is bounded by multiple-layer surface steps on both sides, in two dimensions or 1 + 1 dimensions. At quasi-steady state, the entire top surface grows taller by one layer during one growth period τ, with the starting and the ending top surface morphologies identical. For the terraces below the top layer, the periodic change of the lengths is similar to the layer-by-layer growth of thin film [25]. Shown in Fig. 1(b) and (c) are the expanded views of the boxed area of Fig. 1(a). At time zero, a nucleus of mathematically zero dimension forms on the top layer; and at time τ, the top surface grows taller by one layer and a nucleus forms again on the top; Fig. 1(c). During the time period from 0 to τ, the first step advances so that x_1 becomes zero at time τ_0; Fig. 1(b). As growth continues with time from τ_0 to τ, the surface morphology returns to that at time zero but the entire surface grows one layer taller; Fig. 1(c).

As shown in Fig. 1(b), during the time between 0 and τ there are n monolayer surface steps and n terraces, plus one island above the n-th terrace. Accordingly, there are $n + 1$ lengths x_1, x_2, …, x_n, and x_t, characterizing the dimensions of the terraces and the top island. There are also $n + 1$ rate equations that govern the evolution of x_1, x_2, …, x_n, and x_t as a function of time. Solution of the $n + 1$ rate equations with boundary conditions gives rise to the terrace length l_1, l_2, …, and l_n at time zero, in terms of τ_0 and τ; the corresponding l_t is zero. We use the term of boundary condition instead of initial condition here since the condition is not for the start of time. To eliminate τ_0 and τ in the solutions, two additional equations are necessary. One of the two additional equations is for the critical nucleation size during growth, and the other for the mass conservation. Once the terrace lengths – l_1, l_2, …, and l_n – are determined, their sum defines the diameter L_m as $2(l_1 + l_2 \ldots + l_n)$.

2.2. General theory

Our formulations start with the length of the first terrace x_1; in this paper, length is in the unit of atomic diameter. At time zero, the lowest trajectory of source atoms cannot reach below the first terrace. Otherwise, the growth would not be in quasi-steady state, because L_m would continue to increase. As shown in Fig. 2, source atoms that go through AB and AC will contribute to the advancement of the first step. The length of AB is simply x_1. However, the length of AC is Y and it changes with time t. We assume that Y linearly decreases with time and it goes to 0 at τ_0. As we will see later in Section 2.3, under quasi-steady state terrace lengths increase linearly with time, and the longer terraces lead to linear decrease of Y. That is, $Y = (\tau_0 - t)/\tau$. The initial vaule of Y is now a parameter τ_0/τ. Ignoring the inter-step diffusion as in the previous formulations [22], we have:

$$\frac{dx_1}{dt} = \frac{1}{2}\left[-F\cos\theta x_1 - F\sin\theta\frac{(\tau_0 - t)}{\tau}\right] \tag{1}$$

Here, we have assumed that the deposition flux from the left does not reach the terraces on the right side of the nanorod. As shown later in Fig. 3, this assumption is valid for all the terraces except the top two. With the boundary condition that x_1 is 0 at $t \geq \tau_0$, the solution of Eq. (1) is:

$$\begin{cases} x_1(t) = \frac{2\tan\theta}{\tau F\cos\theta}\left[e^{\frac{F\cos\theta(\tau_0 - t)}{2}} - \frac{F\cos\theta(\tau_0 - t)}{2} - 1\right] & \text{if } 0 \leq t < \tau_0 \\ x_1(t) = 0 & \text{if } \tau_0 \leq t < \tau \end{cases} \tag{2}$$

At time zero, when a new layer nucleates on the top island, the length of the first terrace is l_1: