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A Framework of Growing Crystalline Nanorods

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The growth of crystalline nanorods has become a common practice in the absence of a solid framework, in either theoretical or conceptual form. This article presents such a framework and puts it in historical perspective of a broader field of crystal growth. This framework derives from three scientific advancements in crystal growth, with focus on multiple-layer surface steps: (I) the diffusion barrier of adatoms down multiple-layer surface steps, (II) the formation and stability of multiple-layer surface steps, and (III) the dimension of surface facets that are bounded by competing monolayer and multiple-layer surface steps. While this framework has only a partial foundation of theoretical formulation, it is more complete conceptually. As an example of impact, this framework predicts that growth of Al nanorods is not feasible using physical vapor deposition at ambient conditions; this prediction has not been proven wrong by any available experiments.

INTRODUCTION

The growth of crystalline nanorods has become a common practice. The small dimensions make nanorods good candidates for electrodes that enhance catalysis[1] and solar panels that enhance light absorption,[2] as two examples of applications. The process of growing crystalline nanorods can be very simple. Using any physical vapor deposition (PVD) technique, one can arrange the substrate for glancing or oblique angle incidence of flux.[3] Typically, the diameter of crystalline nanorods is on the order of 100 nm (or several hundreds of nanometers) as shown in Fig. 1,[4] but ultrasmall nanorods with diameter on the order of 10 nm are also possible.[5]

It may be expected that the growth of crystalline nanorods follows the established theories or models of crystal growth. But this is not the case. In order to see how the growth of nanorods defies the conventional wisdom, we take a brief look at the status of crystal growth theory. Starting from the classical Burton-Cabrera-Frank (BCF) theory,[6] the two additional developments that are most relevant to the growth of crystalline nanorods are step dynamics[7] and mound formation.[8,9]

Based on the established theories, the growth of crystals can be in the form of smooth films (Fig. 2a) or mounds (Fig. 2b). The growth mode of smooth films can operate either on a flat low-index crystalline surface or on one with a miscut angle. Surface steps, as shown in Fig. 2b, often impose an extra diffusion barrier to adatoms when they go from one terrace to another. This barrier is the Ehrlich-Schwoebel (ES) barrier, discovered in the 1960s.[10,11] The ES barrier triggers mound formation (Fig. 2b), and geometrical shadowing further promotes the growth of mounds. It is tempting to correlate a tall mound with a nanorod and therefore use the theory of mound growth for the growth of nanorods, but such a correlation has proven invalid.[12] By considering the mound formation under the conventional ES barrier, our simulations show that the top facet dimension will be larger than 1,000 nm under typical PVD conditions.[12] This inability to predict the order of magnitude of nanorod dimension provoked us to propose a new model based on the dynamics of multiple-layer surface steps. As shown in Fig. 2c, we propose that top surface facets of crystalline nanorods are bounded by the mixture of monolayer and multiple-layer surface steps.

A model that relies on the dynamics of multiple-layer steps must reconcile with the classical theory of Schwoebel and Shipsey.[11] According to this classical theory, the extra ES barrier or the kinetic effect will prevent monolayer surface steps from clustering into multiple-layer steps in the absence of thermodynamic driving forces such as strain energy. Correction of this part of the classical theory in one of the three scientific advancements will be described in the next section.

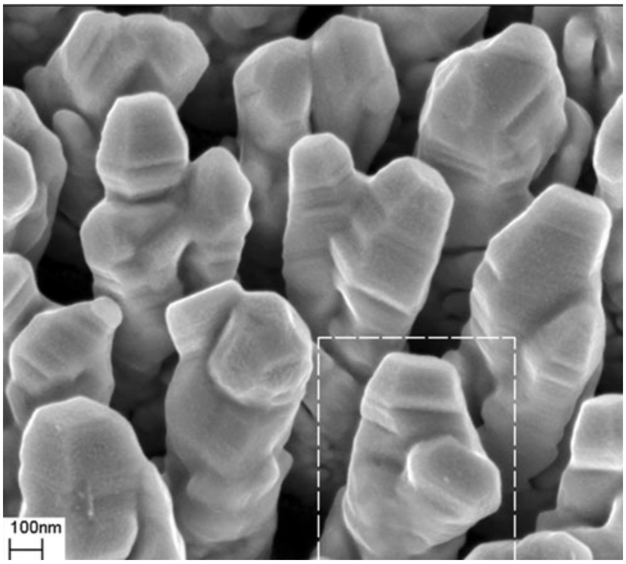

Fig. 1. Scanning electron microscopy image of Cu nanorods (reprinted with permission from Ref. [14]).

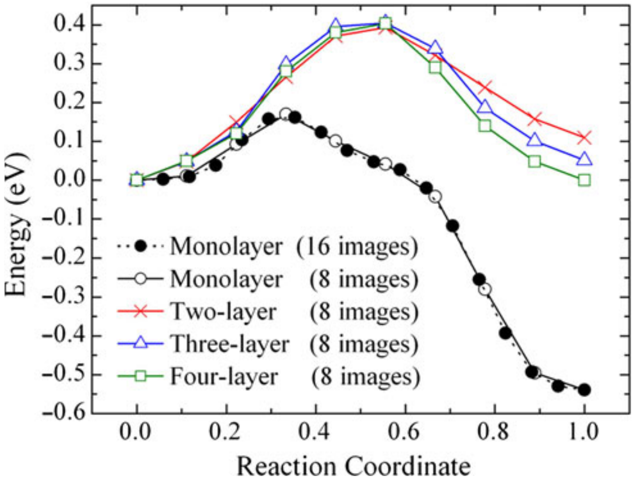

Fig. 3. Quantum mechanics calculation result of energy profile as a Cu adatom diffuses down a surface step from Cu{111} surface (reprinted with permission from Ref. [15]).

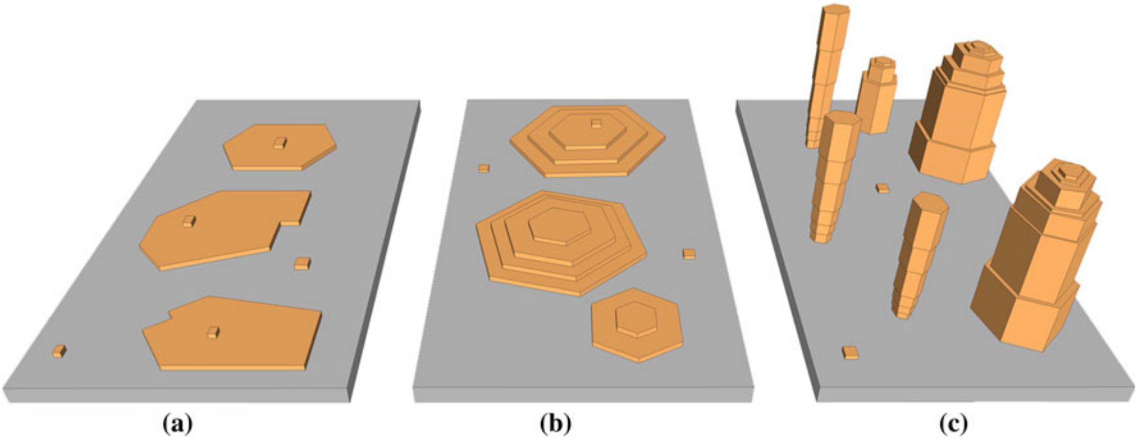

Fig. 2. Schematic of crystal growth in three modes: (a) smooth films, (b) mounds, and (c) nanorods.

THREE SCIENTIFIC ADVANCEMENTS

Before presenting a framework of growing crystalline nanorods, we first review the scientific foundation in terms of three advancements. The three key scientific advancements on the dynamics of multiple-layer surface steps are (I) diffusion of adatoms down multiple-layer surface steps, (II) clustering of monolayer surface steps into multiple-layer surface steps, and (III) characteristic dimension of surface facets that are bounded by a mixture of monolayer and multiple-layer surface steps. These advancements not only allow the reconciliation with the classical theory of Schwoebel and Shipsey but also set the foundation for the framework of growing crystalline nanorods as schematically shown in Fig. 2c.

The first advancement is the recognition that adatoms can experience a much larger diffusion barrier down a multiple-layer surface step than down a monolayer surface step.[13,14] This recognition is an extension of the discovery of ES barrier.[10,11] As a convention, we refer to the total diffusion barrier of an adatom down a multiple-layer step as a three-dimensional (3D) ES barrier and that down a monolayer step as a two-dimensional (2D) ES barrier. As shown in Fig. 3, the 3D ES barrier (0.40 eV) is substantially larger than its 2D counterpart (0.16 eV), and the 3D ES barrier is nearly invariant with the number of layers in a multiple-layer step beyond two layers.

In retrospect, two other papers had touched on this aspect before 2002. In 1986, Bruinsma and Zangwill[16] included a diffusion process down multiple-layer steps (or between two facets) in the schematic figure, even though this process was not included in the formulation. In 2000, Baletto et al.[17] examined the diffusion barrier of adatoms between two facets of a nanoparticle to show that this barrier

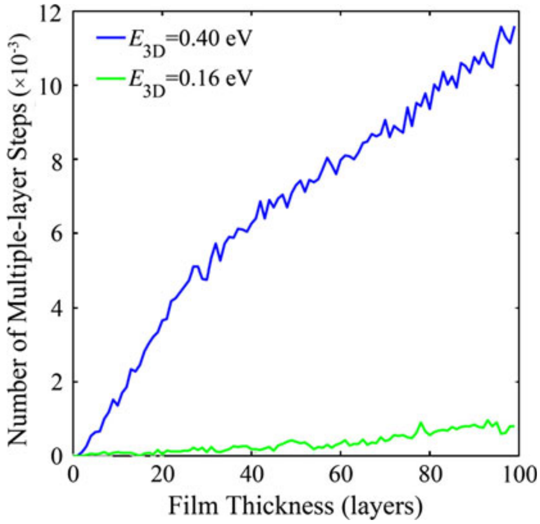

Fig. 4. Number of multiple-layer steps as a function of thickness of a growing film when the 3D ES barrier is taken into account (E_{3D} = 0.40 eV), and when it is not taken into account (E_{3D} = 0.16 eV) (reprinted with permission from Ref. [18]).

is small due to the small size of nanoparticles. The key of the first scientific advancement is that the diffusion barrier of adatoms down multiple-layer surface steps can be substantially larger than down monolayer surface steps. In order for this advancement to be meaningful, multiple-layer steps must be present, in contrast to what the classical theory predicted.[11]

The second scientific advancement is the recognition of mechanisms that stabilize multiple-layer surface steps. By random fluctuation, two monolayer surface steps can cluster into a two-layer surface step. If the 3D ES barrier were the same as that of 2D ES barrier, then the driving force presented by Schwoebel and Shipsey[11] would lead to the dissociation of the two-layer step. However, when the 3D ES barrier is larger than the 2D ES barrier, fewer adatoms will be able to diffuse down the two-layer step, slowing down its dissociation. Also because of the larger 3D ES barrier, the terrace above the two-layer step accumulates more adatoms and is filled up faster, promoting the growth of the two-layer step into three layers. As a result of these two mechanisms, the number of multiple-layer steps increases fast during the growth of a Cu film, as demonstrated in Fig. 4. If the 3D ES barrier is reduced to its 2D counterpart (from 0.40 eV to 0.16 eV), then the number of multiple-layer surface steps is an order of magnitude smaller.

Interestingly, the function of 3D ES barrier also promotes the stability of multiple-layer surface steps, and the stability of multiple-layer surface steps in turn allows the function of the 3D ES barrier. This positive feedback enables the self-sustainability of multiple-layer surface steps once they are formed through random fluctuations.

The third scientific advancement is the discovery of a new characteristic length scale. From the first two advancements, it is clear that multiple-layer steps can be stable and they pose large diffusion barriers to adatoms. The kinetics of diffusion transport across the multiple-layer surface steps defines a characteristic length scale of growing crystalline nanorods L_{3D}; in contrast, for monolayer surface steps, the length scale is L_{2D}. As shown in Fig. 5, the top surface facet (which may contain monolayer surface steps are therefore not precisely atomic flat facets) of a growing crystalline nanorod is bounded by both multiple-layer and monolayer surface steps; here, two multiple-layers surface steps are shown to emphasize their effects. As the multiple-layer surface steps become more dominant, the characteristic length scale L_{3D} becomes smaller. The degree of dominance of multiple-layer steps depends on deposition conditions and material type, as discussed in the next section.

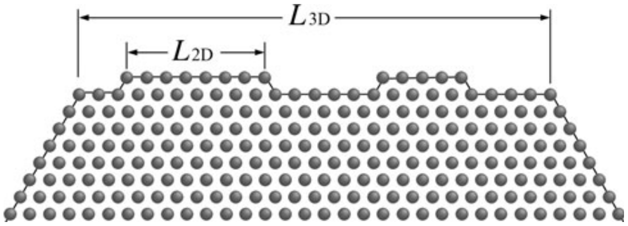

Fig. 5. Schematic cross-section of a top surface facet of a growing crystalline nanorod, with two length scales L_{3D} and L_{2D} highlighted (reprinted with permission from Ref. [19]).

FRAMEWORK OF GROWING CRYSTALLINE NANORODS

Through synergizing the three scientific advancements, we first develop a conceptual framework of growing crystalline nanorods and then develop a theoretical framework that quantifies the growth process. At this point, the conceptual framework—through a combination of atomistic simulations, PVD experiments, and available theoretical formulations—is logically complete. However, the theoretical formulation is complete only in terms of the lower limit of L_{3D} and the approximate expression of L_{3D} in general, *together* with a limiting length scale—the separation of nanorods by nucleation. The dynamics of multiple-layer surface steps couples closely with the length scales, and its theoretical foundation is still being formulated.

In the following, the description of the framework will be primarily conceptual, with discussions of theoretical formulations in terms of numerical results only. As shown in the first figure of this paper, Fig. 2 (particularly Fig. 2c), two modes of growth are possible. In the first mode, a nanorod can start from a wetting substrate and first nucleate a mound. During the growth, the number of multiple-layer surface steps increases, and the top facets become smaller due to the 3D ES barrier. At a quasi-steady state, the top of the nanorods remains self-similar as deposition continues. The balance of

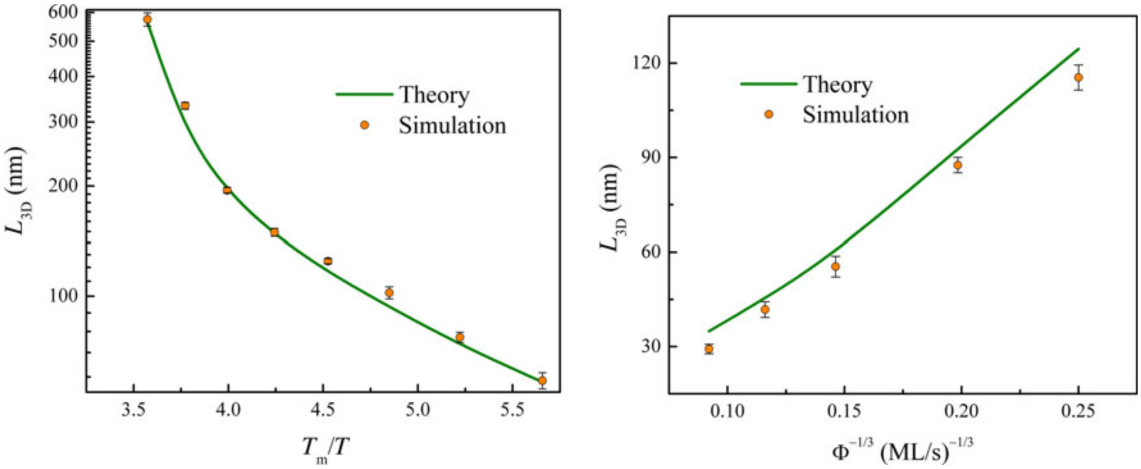

Fig. 6. Characteristic length scale L_{3D} as a function of homologous temperature T/T_m and deposition rate Φ for Cu (reprinted with permission from Ref. [19]).

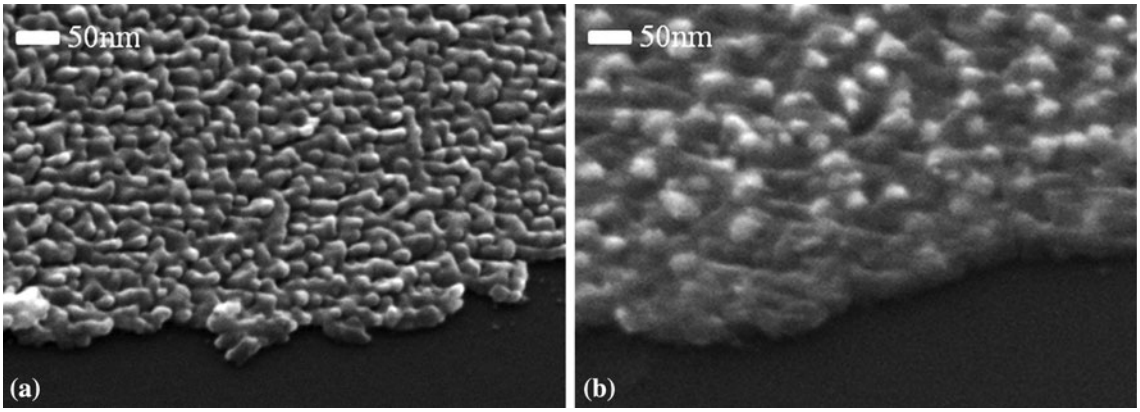

Fig. 7. Scanning electron microscopy image of (a) Cu nanorods of about 30 nm in diameter and (b) Cu film at higher deposition rate than in (a) (reprinted with permission from Ref. [5]).

atomic flux across the surface steps that bound the top facet defines a characteristic length scale; the surface steps change between monolayer and multiple-layer in nature. As shown in Fig. 6, both theoretical formulations and atomistic simulations show that the characteristic length scale L_{3D} is on the order of 100 nm under typical PVD conditions. The dimension of top surface facet L_{3D} is not the same as the diameter of a nanorod, but the two dimensions are on the same order of magnitude. By the first mode of growing crystalline nanorods, the diameter is on the order of 100 nm as commonly seen (such as Fig. 1). Reduction of this to the order of 10 nm would require an extremely low substrate temperature or extremely high deposition rate.

The second growth mode in Fig. 2c offers a mechanism of reaching smaller L_{3D} and thereby diameter of crystalline nanorods. Starting from a nonwetting substrate, a nanorod nucleus is a multiple-layer island. Due to the nonwettability, adatoms accumulate to the top of island, resulting in an initially smaller diameter than the final quasi-steady state value. As deposition proceeds, the island grows both vertically and horizontally to reach the quasi-steady state diameter. Because the nanorod diameter starts small, the morphology of this nanorod naturally requires stronger dominance of multiple-layer surface steps around the top surface facets. At an idealized limit of perfect geometrical shadowing and 100% multiple-layer surface steps that bound the top surface facet, our theoretical formulation shows that L_{3D} is on the order of 10 nm.[20] Using atomistic simulations of more realistic PVD conditions, we show that the lower limit of L_{3D} is on the order of 30 nm. This is also consistent with the competition between the diameter of nanorods and the separation of nanorods.[19] If the separation becomes smaller than the diameter, even if both are small, then nanorods will not be sustainable and will merge to form a dense film. As shown in Fig. 7, experiments indeed confirm that the smallest Cu nanorods are on the order of 30 nm in diameter. Further attempts to reach even smaller nanorods by increasing deposition rate result in a dense film.

To show the impact of this framework of growing crystalline nanorods, we pick an example of Al versus Cu. The two metals are comparable in many aspects such as their melting temperature and elastic properties. Due to partial covalent bonding, the 3D ES barrier of Al is small, and multiple-layer surface steps are unstable. As a result, the growth of Al nanorods using PVD at ambient conditions is not feasible according to the framework; in contrast, this is feasible for Cu nanorods. Numerous reports of Cu nanorods confirm the feasibility of growing Cu nanorods using PVD. The prediction of infeasibility of growing Al nanorods by PVD at ambient conditions has not been proven wrong by any experiments thus far.

SUMMARY

This article has presented a framework of growing crystalline nanorods. This framework derives from the synergy of three advancements in crystal growth—stability of multiple-layer surface steps, diffusion barrier of adatoms down multiple-layer steps, and characteristic dimension of surface facets bounded by monolayer and multiple-layer steps. These three advancements are the result of theoretical formulations, atomistic simulations, and PVD experiments.

The dynamics of multiple-layer surface steps separates this framework from existing theories/models of crystal growth. In contrast to the classic theory of Schwoebel and Shipsey,[11] we have shown that multiple-layer surface steps can be kinetically stabilized. Furthermore, we have shown that the diffusion barrier of adatoms down multiple-layer surface steps can be substantially larger than that down monolayer surface steps. The competition of monolayer and multiple-layer surface steps gives rise to a new characteristic length scale, the dimension of surface facets. Under typical PVD conditions without a nonwetting substrate, this dimension is on the order of 100 nm. With a nonwetting substrate, this dimension can be as small as about 10 nm.

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