



Review

Synergy to discovery and innovation – Growth of nanorods

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HIGHLIGHTS

- Synergy of atomistic simulations, analytical formulations, and experiments is described and demonstrated in the study of nanorod growth.
- As one demonstration, the discovery of smallest and well-separated nanorods becomes possible.
- As another demonstration, the innovation of metallic glue technology comes to light.

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ABSTRACT

A synergy of computer simulations, analytical formulations, and experiments proves very effective in research and development. Using nanorod growth as an example, this letter presents the synergy of the three complementary approaches in research, and demonstrates its effectiveness. Through this synergy, a theoretical framework of nanorod growth emerges; through the direction of the theories, experimental realization of smallest well-separated nanorods becomes reality; through the realization of such nanorods, metallic glue in ambient environments becomes technical reality and commercial possibility.

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Contents

1. Introduction.....	249
2. Synergy.....	250
3. Summary.....	251
Acknowledgments.....	251
References.....	252

1. Introduction

Nanorods are rods, pillars, or columns with a lateral dimension on the order of tens of nanometers. Their aspect ratio is typically on the order of 10 or smaller; if the aspect ratio is larger, they are generally called nanowires. Growth of nanorods is feasible through various approaches, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and solution processing [1–3]. PVD is the cleanest and most controllable process. Once the PVD process is well understood, one may include additional chemical

reactions and solid–fluid mechanics to understand other growth processes that are more complex. Therefore, we take the PVD process as the prototype for scientific understanding of nanorod growth.

Within the framework of PVD, nanorod growth relies on the glancing angle deposition technique or geometrical shadowing effects [4,5]. In connection with thin film depositions, the nanorods bear some similarities with porous films except that nanorods are better separated. In addition to geometrical shadowing, nanorod growth also relies on limited diffusion at low temperatures, typically below $0.3T_m$ (30% of the melting temperature).

Theories exist for thin film deposition at the continuum level [6], nucleation and growth at the atomic level [7], and growth of roughening surfaces with Ehrlich–Schwoebel (ES) barriers [8–11]. However, these theories do not apply to the growth of

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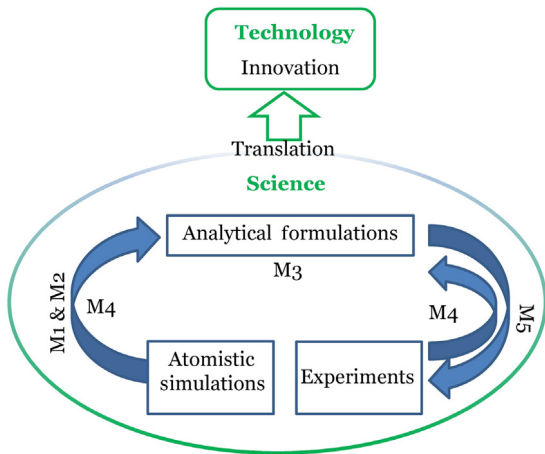


Fig. 1. Flow chart of synergy, showing the five milestones from M1 to M5.

nanorods. Even with the ES barrier taken into account, characteristic length scales of surfaces are on the order of a micron according to the existing theories. In contrast, nanorods from PVD experiments are as small as a few nanometers and typically on the order of tens of nanometer. In order to design nanorod growth, it is essential to understand what mechanisms control the growth process and to establish a theoretical framework. Achieving this goal requires or at least benefits from the synergy of atomistic simulations, analytical formulations, and experiments.

2. Synergy

Throughout our studies of nanorod growth, five milestones of scientific discoveries have been pivotal: (1) the discovery of the large diffusion barrier over multiple-layer surface steps, (2) the identification of an error in the classical theory that when corrected establishes the kinetic stability of multiple-layer surface steps, (3) development of theories for nanorod diameter and nanorod separation, (4) verification and validation of the theories, and (5) theory-guided design of experiments. As shown in Fig. 1, these five milestones involve atomistic simulations, analytical formulations, experiments, and more importantly their synergy. As translation of the scientific discoveries, metallic glue technology represents an innovation. This section describes each of the five milestones and the translation, highlighting the synergy of methods.

The first breakthrough in our understanding of nanorod growth is the identification of the large diffusion barrier over multiple-layer surface steps through atomistic simulations including both classical molecular statics and density-functional-theory calculations. On the foundation of the wedding cake model [10,11], it is possible to understand characteristic length scales of surfaces on the order of a micron or a fraction of a micron during PVD. However, the diameter of nanorods from PVD experiments is at least an order of magnitude smaller. The order-of-magnitude difference between existing theories and experiments calls for the discovery of missing mechanisms. Using interatomic potential based molecular statics calculations, we have brought to light the critical role of diffusion of adatoms over multiple-layer surface steps, which had been overlooked. According to our calculations, the diffusion over multiple-layer surface steps can be 100000 times slower than over monolayer surface steps at room temperature [12,13]. As shown in Fig. 2, for a Cu {111} system that contains an adatom, the total energy increases and then decreases as an adatom diffuses from start to end (diffusion coordinate from 0 to 1). The diffusion barrier of Cu adatoms increases from 0.16 eV to 0.40 eV as the steps go from monolayer to two or more layers.

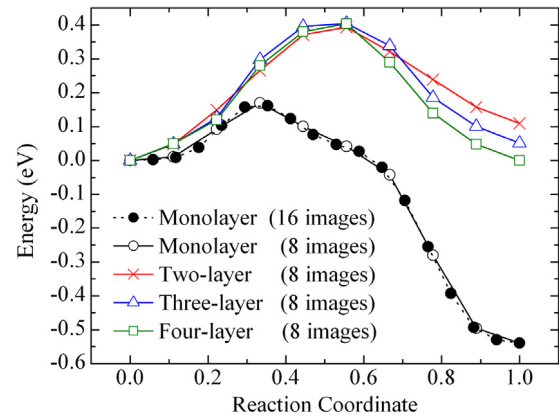


Fig. 2. Energy of a Cu system as a function of reaction coordinate along the diffusion path of an adatom. Source: Reprinted with permission from Ref. [13].

A dilemma was realized soon after the discovery of the large diffusion barrier of adatoms over multiple-layer surface steps. On the one hand, this large diffusion barrier offers a potential explanation for the order-of-magnitude smaller diameter of nanorods in experiments. On the other hand, this large diffusion barrier cannot function according to the classical theories. In the publication in 1966 [9], Schwoebel and Shipsey analytically showed that multiple-layer surface steps would not be stable kinetically. In nanorod growth process, thermodynamic driving forces such as strain energy are absent due to the small dimensions. If the classical theory prevails, the discovery of the large diffusion barrier is meaningless since multiple-layer surface steps are not stable. Another atomistic simulation method came to the rescue: the lattice kinetic Monte Carlo (LKMC) method. Using LKMC simulations, we have shown that a positive feedback mechanism stabilizes multiple-layer surface steps. By random fluctuations, two or more monolayer steps can bunch to form a multiple-layer step. Once formed, the large diffusion barrier of the multiple-layer step enhances its stability by reducing the chance of dissociation [14]. Geometrical shadowing in glancing angle deposition, which is generally used for nanorod growth, further stabilizes multiple-layer surface steps. This advancement enriches and corrects the classical theory, and more importantly takes us further along the way of understanding nanorod growth.

Now that the large diffusion barrier of adatoms over multiple-layer surface steps is shown to exist and to function, a characteristic surface length scale should exist in connection with this barrier. The diameter of nanorods depends on the nature of steps that bound the top surface. If the steps are multiple-layer, instead of monolayer, the diffusion barrier is large and therefore the diameter is small. When the steps are 100% multiple-layer in nature, the diameter is the smallest. Our analytical formulations [15] show that the smallest diameter of nanorod L_{\min} is

$$L_{\min} = [(10/\alpha^2) \ln(n/2)(v_{3D}/F_e)]^{1/5}.$$

Here the diffusion jump rate v_{3D} is an Arrhenius function of the diffusion barrier of adatoms over multiple-layer surface steps, F_e is the effective deposition rate over the top surface, α is a geometrical factor of the top cross section of the nanorod and it is on the order of one, and n is the height of nanorod that remains in cylindrical shape and typically is on the order of 2000 for Cu. It is important to recognize that the analytical formulations rely on idealized assumptions; for example, the cross section of nanorods is assumed circular, and it is rarely the case for crystalline nanorods. Using LKMC simulations, we have verified the analytical theory of L_{\min} , and shown that the idealized assumptions cause only minor errors. This verified theory allows us to understand why the order

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