Communication

A theoretical model describing the one-dimensional growth of single crystals on free sustained substrates

Ziran Ye [a,b], Ke Wang [a], Chenxi Lu [c], Ying Jin [c], Chenghua Sui [a,b], Bo Yan [a,b], Fan Gao [a,b], Pinggen Cai [a,b], Bin Lv [a,b], Yun Li [a,b], Naibo Chen [a,b], Guofang Sun [a], Fengyun Xu [a], Gaoxiang Ye [c,*]

[a] Department of Applied Physics, College of Science, Zhejiang University of Technology, Hangzhou, China
[b] Center for Optics & Optoelectronics Research (COOR), Collaborative Innovation Center for Information Technology in Biological and Medical Physics, College of Science, Zhejiang University of Technology, Hangzhou, China
[c] Department of Physics, Zhejiang University, Hangzhou, China

ARTICLE INFO

ABSTRACT

We develop a theoretical model that interprets the growth mechanism of zinc (Zn) crystal nanorods on a liquid substrate by thermal evaporation. During deposition, Zn atoms diffuse randomly on an isotropic and quasi-free sustained substrate, the nucleation of the atoms results in the primary nanorod (or seed crystal) growth. Subsequently, a characteristic one-dimensional atomic aggregation is proposed, which leads to the accelerating growth of the crystal nanorod along its preferential growth direction until the growth terminates. The theoretical results are in good agreement with the experimental findings.

1. Introduction

The understanding and controllable growth of single crystals on a variety of substrates are of particular interest [1–3]. Experiments on the growth of crystals have been thus far mainly performed on various solid and liquid substrates [4,5], among which one-dimensional nanostructures have received enormous attention due to their applied potential in fabricating new types of optoelectronic, nanoelectronic, or electromechanical devices [6,7]. Current research interest focuses on the understanding of the growth mechanism of one-dimensional nanostructures with desired size and morphology, in which Vapor-liquid-solid (VLS) [8] and Solution-Liquid-Solid (SLS) [9] mechanisms are the two well-established growth models of the one-dimensional nanostructures on liquid-solid interface. Although these approaches are relatively effective and controllable, such processes are usually catalyst-assisted and conducted under high temperatures [10,11].

In principle, since a liquid surface possesses isotropic and quasi-free sustained characteristics, metallic atoms may diffuse randomly on the liquid substrate with large diffusion coefficients compared with that on solid substrates [12]. Therefore, after nucleation and aggregation, metallic compact clusters and ramified aggregates with amorphous or polycrystalline microstructures [13] are usually obtained on the liquid substrates. The whole process is generally described by the two-stage growth model [12].

Recently, it has been shown in our experiment that, by choosing appropriate experimental conditions, Zn crystal nanorods with different lengths, widths and thicknesses may also be prepared on the liquid surface at room temperature by thermal evaporation method [14]. This anomalous growth process of one-dimensional (or to be more exact, quasi one-dimensional) Zn crystals can be considered as an exception to the two-stage growth model [12]. Therefore, it is necessary to understand the underlying mechanism involved in such catalyst-free growth behavior on the isotropic and free sustained substrates.

In this paper, we develop a new theoretical model to interpret the growth mechanism of the Zn crystal nanorods on liquid surfaces. The growth process of a nanorod on the isotropic and free-sustained substrate may be divided into two periods: (1) the nucleation and primary nanorod (or seed crystal) formation during Zn deposition, and (2) a characteristic one-dimensional atomic aggregation and then the growth of the crystal nanorod along its preferential growth direction [8,9,14]. It is proposed that the seed crystal generates at the very initial growth stage, and the characteristics of the preferential growth direction of Zn crystals and the fast diffusion rate of Zn atom on the free-sustained liquid surface are the two vital reasons for the Zn crystal nanorod growth.

2. Experiment description and hypotheses

The Zn nanorods were catalyst-freely prepared on silicone oil surface at room temperature by thermal evaporation method [14]. Transmission electron microscope (TEM) measurement was performed to understand the microstructure of the Zn nanorods, in which lattice fringes can be observed clearly, indicating the crystal structures; the selected-area Diffraction patterns of the Zn nanorods further confirms that the nano-rods are single crystals; Therefore, the experimental results show that the one-dimensional Zn crystals, i.e., the Zn crystal nanorods, really grow on the oil surface along [002] (*c*-axis) direction, the preferential growth direction of the hexagonal structure crystal, at room temperature [14].

Generally, a liquid surface may be considered as a quasi-free sustained substrate and it usually possesses isotropic characteristics. The experimental phenomenon is quite interesting since it indicates that the oriented crystal growth on the isotropic surface is exactly possible. The growth mechanism of the nanorods on the liquid surfaces may be qualitatively explained by a combination of two effects: the liquid sub-strate effect, which prevents large internal stress, strong adatom-substrate interaction and lattice mismatch, and the characteristics of the preferential growth direction of the hexagonal crystal [14].

In order to establish a theoretical model for the growth mechanism of the Zn crystal nanorods, based on the experimental results above [14], several hypotheses are proposed as follows:

1. Zn atoms diffuse and aggregate on an isotropic and free sustained liquid surface randomly with large diffusion coefficient [12]. Then they nucleate and seed crystals form.
2. The diameter of the Zn crystal nanorod is determined by the growth behavior of the seed crystal instead of the catalyst particle size in VLS and SLS models [8,9].
3. During deposition, the nanorod grows on the oil surface along [002] (*c*-axis) direction, the preferential growth direction of the hexagonal structure crystals [8,9,14].
4. The mass supply to the nanorod growth is mainly attributed to the diffusion of the neighboring Zn atoms in the diffusion area around the nanorod.
5. The aggregated atoms may diffuse on the nanorod surface along its preferential growth direction until the lowest free energy is reached, which results in the formation of the Zn crystal nanorod.

3. Theoretical model and results

The overall growth process of Zn crystal nanorods is proposed as the initial Zn seed crystals generated in a very short time after Zn atoms "landed on" the liquid surface, following by the subsequent growth along *c*-axis. Based on the time sequence, during deposition, Zn atoms diffuse randomly on an isotropic and quasi-free sustained substrate and the nucleation of the atoms results in the primary nanorod (or seed crystal with size a_0) growth. Subsequently, a characteristic one-dimensional atomic aggregation starts, which results in the growth of the crystal nanorod along the preferential growth direction until the growth terminates.

Here we define λ as the effective diffusion length on the crystal nanorod surface [8,9], D as the diffusion coefficient of the Zn atoms on the liquid surface, t as the deposited time, x as the length of the nanorod, $r(t)$ as the radius of the nanorod at given time, and $r0 = w/2 =$ constant, where w is the final diameter of cross-sectional area of the nanorod. Based on the experiment, we let the deposition rate $f = 0.01$ nm/s below. It is suggested that $R^2 \sim <\Delta r^2> = 4D\Delta t$ [12,15,16], where $<\Delta r^2>$ is the mean square diffusion displacement of the Zn atoms and Δt is the diffusion time interval. Here $R \gg r_0$ in our experimental conditions.

3.1. At initial growth stage (a_0 x r_0)

In case of $a_0 < x < r_0$, namely stage I, both the radius r and length x are small. After nucleation and at the growth beginning, $t = 0$ and a seed crystal is formed with $r(0) = x(0) = a_0$. Then it starts to grow, the radius and length of the crystal nanorod varies over time, which can be written as $r = r(t)$ and $x = x(t)$, respectively. During this time scale, two growth pathways occur simultaneously, one is along the direction of the radius r and the other is along the nanorod length x (*c*-axis), as shown in Fig. 1. Here we introduce another factor σ as the percentage of Zn atoms which participate in the growth of Zn nanorod length x along the *c*-axis, and the rest of the Zn atoms mainly contribute to the growth of the radius r. This assumption is different from that of the catalyst-assistant method, in which the size of the metal catalyst particle determines the diameter of the one-dimensional nanostructure [8,9].

According to the hypotheses above, during deposition, the mass supply to the nanorod growth is mainly attributed to the diffusion of the neighboring Zn atoms in the diffusion area around the nanorod, as shown in Fig. 1, which may be divided by 4 parts, namely area 1, area 2, area 3 and area 4.

Area 1 (two rectangles) represents the substrate area surrounding the Zn nanorod and all the Zn atoms deposited in this area during time dt will aggregate to the nanorod, which can be expressed as the term of $2Rxfdt$. The Zn atoms in area 2 (a semi-circle) deposited during time dt and the Zn atoms in area 3 (semiring area) deposited during time t (rather than dt) will aggregate to the tip of the nanorod when it grows dx along the *c*-axis, which can be written as $\frac{1}{2}\pi R^2 fdt + 2Rftdx$. The total amount of Zn atoms con-tained in the actual extended Zn nanorod should equal $\pi r^2 dx$. Thus, based on the mass balance consideration, one can have the following equation:

$$\sigma 2Rxfdt + \frac{1}{2}\pi R^2 fdt + 2Rftdx = \pi r^2 dx \tag{1}$$

Besides, the rest part of deposited Zn atoms in area 1, i.e., $(1 - \sigma)2Rxfdt$ will result in the expansion of the seed crystal radius r, which can be written as $2\pi r dr x$. Then the second mass balance equation can be written as:

$$(1 - \sigma)2Rxfdt = 2\pi r dr x \tag{2}$$

From Eq. (1) and Eq. (2), one can have

$$x = \frac{a0 + \frac{\pi R}{4\sigma}}{1 - \frac{t}{t1}} - \frac{\pi R}{4\sigma} \tag{3}$$

and

$$r^2 = a_0^2 + \frac{2(1 - \sigma)Rf}{\pi} t, \tag{4}$$
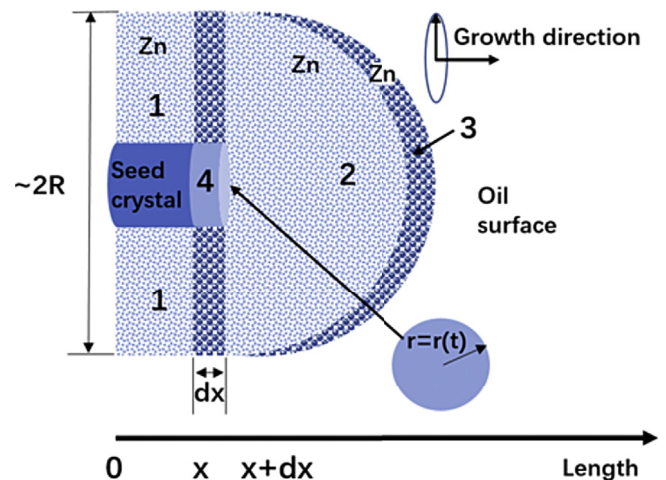
Where $t1 = \frac{\pi a_0^2}{2Rf\sigma}$.

Fig. 1. Schematic illustration of Zn nanorod growth when $a_0 < x(t) < r_0$ and $r = r(t)$.