A diffusion-controlled kinetic model for growth of Au-catalyzed ZnO nanorods: Theory and experiment

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Abstract

A kinetic model for growth of ZnO nanorods via vapor–liquid–solid (VLS) mechanism based on the bulk diffusion of Zn atoms through the Au–Zn droplet is presented. The dependences of the growth rate on size are given quantitatively. A general expression for the growth rate of nanorods during VLS process is derived. The derived formula shows the dependences of growth rate on lateral size of nanorods, concentration and supersaturation of Zn atoms in the liquid droplet. Based on the presented kinetic model the smaller nanorods have faster growth rate. Au-catalyzed ZnO nanorods are grown by chemical vapor transport and condensation (CVTC) process experimentally. Theoretical and experimental rate/radius curves are compared to each other. Theoretical predictions are in good agreement with the experimental results.
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1. Introduction

One-dimensional ZnO nanostructures are key functional materials in nanotechnology [1–3]. Recently, there has been considerable interest in synthesis methods of ZnO nanorods based on the vapor–liquid–solid (VLS) mechanism [4–13]. The VLS theory was first proposed by Wagner and Ellis [14] for Si whiskers in the presence of Au particles. There are three main models explaining the transportation processes of atoms and growth in the VLS mechanism [15]. In the first model, a liquid alloyed droplet initiates and guides the growth and acts as a preferential site for adsorbing incoming atoms from vapor phase [4,15,16]. Nanorod growth begins after the liquid droplet becomes supersaturated and solid nanorod is formed by precipitation from droplet [16,17]. In the second model, incoming atoms diffuse on the droplet surface to the liquid/solid interface where they are attached to the solid nanorod [15].

In the third model, it is assumed that incoming atoms impinge on the whole nanorod surface and diffuse along it to the droplet interface [15]. Based on these models, growth may be limited by interface reactions, diffusion, or both [15–17].

It is well known that the growth rate is affected by the lateral size of nanorod [15,18–21]. There are several studies covering the theoretical and experimental results of the radius dependence of nanorod growth rate [15,18–28]. In the interface reaction controlled VLS growth, nanorods with larger radius grow faster than those with a smaller radius due to the capillarity effect [15,21]. In contrast, it has been shown that growth rate is inversely proportional to the radius for some materials such as CVD-grown Si whiskers [15], GaP nanowires [18], magnetron sputtering-deposited GaAs nanowires [23], MOVPE-grown InAs [26,27], and MBE-grown Si whiskers [28]. An expression in the general form $\mathrm{d}l/\mathrm{d}t = C/R$ (C is constant) has been reported by Schubert et al. [15]. Recently, several theoretical models have been developed for describing $1/R$ dependence of nanowires growth rate [19,23–25].

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However, the growth kinetics of oxide nanorods such as ZnO is not understood very well, and there are many unexplained phenomena and inconsistencies in the current theories due to presence of oxidizing species.

The aim of this work is theoretical and experimental investigation of Au-catalyzed ZnO nanorods formation during chemical vapor transport and condensation (CVTC) process. A diffusion-controlled kinetic model of ZnO nanorods growth will be presented based on the VLS conceptual model which we presented in Ref. [17]. A general expression for growth rate will be derived which will explain the dependences of growth rate on diameter of nanorods and growth conditions. Comparisons will be made between experimentally obtained values of the ZnO nanorods growth rate and those computed using derived formula in this work.

2. Theoretical model

Major processes involved in the VLS mechanism of ZnO nanorods are adsorption–desorption on the droplet surface, transportation of Zn atoms, condensation and oxidation of Zn atoms at growth front [17]. Two potential candidates for the limiting process of the VLS growth are the processes at the vapor–liquid interface (unlikely case) and processes in the volume of liquid droplet (likely case) [21]. In the case of ZnO nanorods, because of high condensation–oxidation rate, transportation of Zn atoms through the droplet is a limiting process. Thus, we can assume that the VLS growth of ZnO nanorods is diffusion-controlled growth, and local equilibrium at the growth front can be supposed. We will publish details of controlling processes in the VLS mechanism of ZnO nanorods in future.

Consider a nanorod of radius R, growing due to the nucleation of the two-dimensional disc-shaped island of height h and radius r. Lateral growth of each island takes place by adding Zn atoms to the ledge of island and simultaneous oxidation of added atoms [17]. Due to this mechanism, the lateral growth rate (u) does not depend on r. The nuclei also can be assumed to arise with zero size [22]. Two nucleation modes under drop can be assumed. In the first mode of nucleation a single nucleus grows and covers the area under the droplet before the next nuclei is formed as shown schematically in Fig. 1(a). This situation relates to the so-called monocenter regime of nucleation [22,29]. A disk-shaped nucleus is grown by lateral movement of its linear ledge of height h. Due to diffusion-controlled growth, local equilibrium against the moving ledge can be assumed. Because of the Gibbs–Thomson effect, the equilibrium concentration (C_e) in the droplet adjacent to the nuclei ledge will be increased to C_r. The concentration profile across the moving ledge will appear as shown in Fig. 1(b). The origin of the driving force for island ledge migration into liquid droplet is shown in Fig. 1(c).
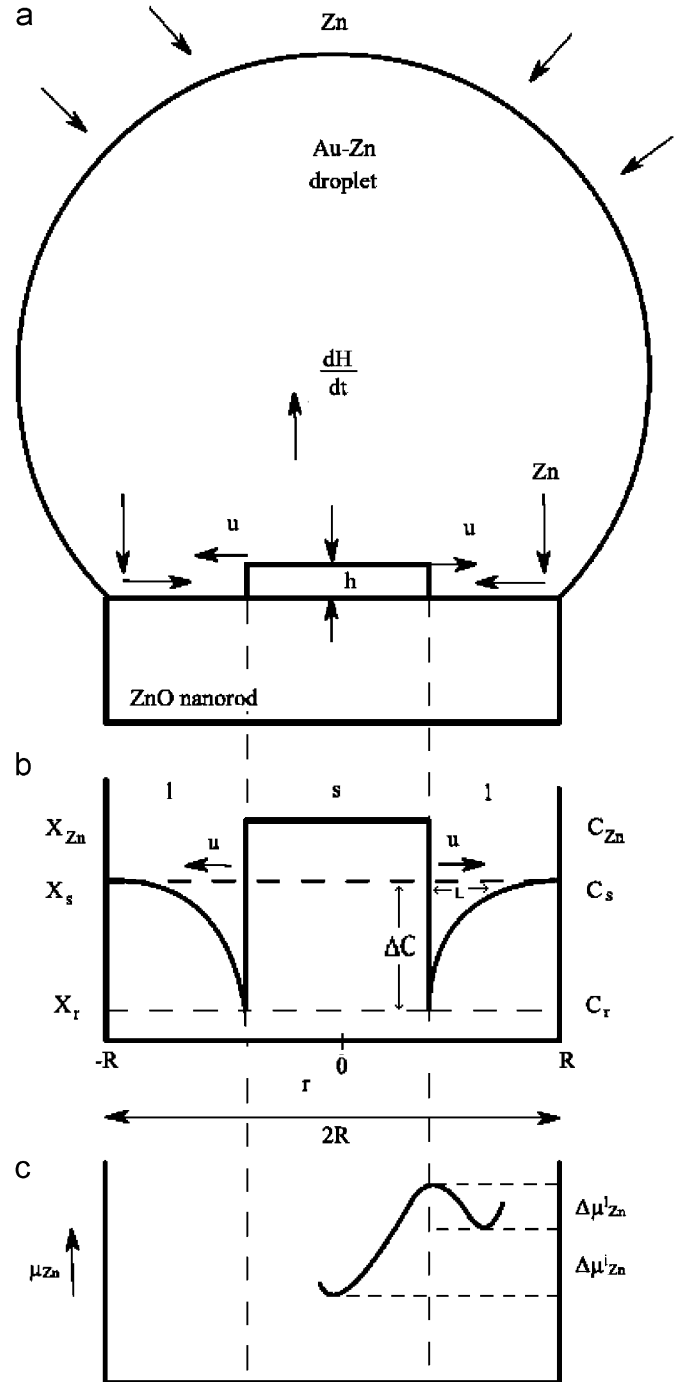

Fig. 1. (a) Schematic illustration of the monocenter regime of nucleation and growth of ZnO nanorods during vapor–liquid–solid (VLS) mechanism as a diffusion-controlled process. (b) Concentration profile across the moving linear ledge of nucleus. (c) The origin of the driving force for island ledge migration into the liquid droplet.

Fig. 1(b) shows that the ledge growth rate (u) will depend on the concentration gradient at the interface (dC/dr). For nuclei ledge of height h and radius r (Fig. 1(a)) to advance a distance dr, a volume of material "$2\pi r h\,\mathrm{d}r$" must be converted from liquid droplet containing C_r to solid ZnO containing C_{Zn} moles of Zn per unit volume. In other