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The mechanism of ZnO nanorod growth by vapor phase transportation

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ABSTRACT

We studied a kinetic model of the ZnO nanorod (NR) growth that occurs via vapor phase transportation (VPT). The mechanism of ZnO NR growth was discussed in terms of the length-to-diameter (*L*–*D*) relationship of NRs, and it was confirmed by varying both the type of catalyst and source material used. Both theoretical calculations and experimental data indicated that elongation of NRs is primarily determined by diffusion of the absorbed atoms (adatoms) within a nominal migration length on the surface, which is not considered in the simple vapor–liquid–solid model.

1. Introduction

One-dimensional (1D) nanostructures, such as nanotubes, nanowires and nanobelts, have attracted considerable attention because of their interesting physical properties and various potential applications [1–5]. Among the 1D semiconductor nanostructures, ZnO nanorods (NR) are of particular interest for application to optoelectronic nanodevices due to their unique properties, such as a large exciton binding energy. Several methods have been employed to synthesize 1D ZnO nanostructures [6–9]. In particular, ZnO NRs are often grown via a catalyst-assisted vapor–liquid–solid (VLS) mechanism. During growth, the catalyst absorbs the vapor components, such as Zn (vapor) and Zn_xO ($x<1$, vapor), to form a eutectic alloy. When the catalyst becomes supersaturated, crystallization and growth occur [10,11]. Therefore, the diameter of the catalyst in the liquid phase determines the diameter of the NR, and the amount of growth species supplied determines NR length. Consequently, there is a linear relationship between NR length and diameter because liquid catalysts with larger diameters absorb more of the growth species than catalysts with small diameters. However, this mechanism does not account for the role of adatoms that are outside the eutectic catalyst. Thus, the ability to control the diameter of the eutectic catalyst is essential for regulation of NR growth. However, there are many examples of previously reported results that cannot be explained by the simple VLS mechanism. For example, growth of ZnO NRs has been reported to occur via a self-catalyzed VLS mechanism [12]. The results of the aforementioned study suggest that during the initial stage of NR growth, either a Zn or ZnO_x droplet formed and subsequently acted as a catalyst. A vapor-solidification (*VS*) mechanism has been reported as another potential mechanism by which ZnO NR growth occurs. The staircase-like morphology of the NRs, which consisted of terraces and steps, was explained by the layer-by-layer growth that occurred on the top of the NRs [13]. These earlier studies provide strong evidence that adatom kinetics have a significant effect on both length–diameter relationship and the morphology of NRs. Since the controlled synthesis of NRs requires a clear understanding of the growth mechanism, studies of the NR growth mechanism are necessary.

The aim of the present study was to investigate the mechanism of ZnO NR growth via vapor phase transportation (VPT). The effects of both types of catalyst and the presence of impurities on the growth mechanism will be discussed in terms of the length–diameter (*L*–*D*) relationship of NRs.

2. Experimental

ZnO NRs can be grown by means of various methods, including metal organic vapor phase epitaxy (MOCVD), molecular beam epitaxy (MBE), physical vapor deposition, hydrothermal

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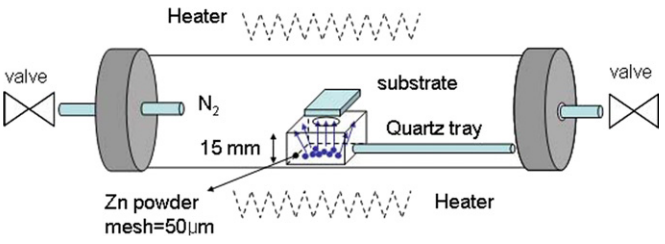

Fig. 1. Schematic drawing of an experimental set-up.

processes, and so on. Among these methods, growth of ZnO NRs by vapor phase transportation (VPT) in a horizontal tube furnace is the simplest and most widely used method (Fig. 1). In the present study, ZnO and In-doped ZnO NRs were grown on AuGe- and Ti-deposited Si(1 1 1) substrates using a horizontal reaction furnace. The composition x of $Au_{1-x}Ge_x$ was 0.43; hence, the melting temperature was estimated to be 560 °C [14]. As shown in Fig. 1, the source materials, i.e., powder phase Zn (4 N, mesh = 50 μm) and In (5 N, mesh = 50 μm), were loaded into a quartz tray, which had two parts separated by 15 mm: the lower part of the tray was for loading the source material and the upper part was for substrate-loading. The evaporated vapor was supplied to the substrates through a via-hole in the upper part of the tray. When the temperature of the furnace reached the growth temperature (T_g), the quartz tray was inserted into the furnace. The ZnO and In-doped ZnO (ZnO:In) NRs were grown at 625 °C. After 30 min, the quartz tray was ejected and allowed to cool in air. Dry N_2, which was used as the ambient gas, was allowed to flow through the quartz tube at a rate of 500 (ml/min) during growth. The surface morphology of each sample was observed using a Quanta 200 FEG scanning electron microscope (SEM) with a field emission gun. The In concentration in the ZnO:In NRs was determined by auger electron spectroscopy (AES) and energy dispersive spectroscopy (EDX) [15].

3. Results and discussion

Fig. 2 shows SEM images of (a) ZnO NRs/Ti/Si(1 1 1) and (b) ZnO NRs/AuGe/Si(1 1 1); the insets show plain-view images of each sample. Despite the difference in melting temperature between the catalysts, we were able to grow well-aligned ZnO NRs with similar diameters. The lengths and diameters of the NRs were evaluated using the plain- and side-view SEM images, and the results are summarized in Fig. 3. NR length was not linearly correlated with NR diameter. Hence, we concluded that the conventional VLS model could not explain the length-to-diameter (L–D) dependence observed in our results. Furthermore, since T_g (625 °C) was considerably lower than the melting temperature of Ti (1668 °C), nucleation in the Ti-droplet was not expected.

Note that VPT growth supports a long diffusion length, since reductions in kinetic energy on the substrate surface can be neglected. Therefore, the contribution of adatom diffusion to the overall growth of NRs should be carefully investigated. The diffusion-induced (DI) mechanism of NR growth has been thoroughly explained by Dubrovskii et al. [16], and it is worthwhile to consider the fundamentals of their explanation. According to the DI mechanism, the atoms that appear in the drop may come from both the source and the substrate surface due to diffusion. In the steady state, the normal growth rate of a NR dL/dt is given by [16]

$$\frac{\pi R^2}{\Omega}\frac{dL}{dt}=\left(\frac{V-V_s}{\Omega}-\frac{2Cr_l}{\tau_l}\right)\pi R^2+j_L \qquad (1)$$

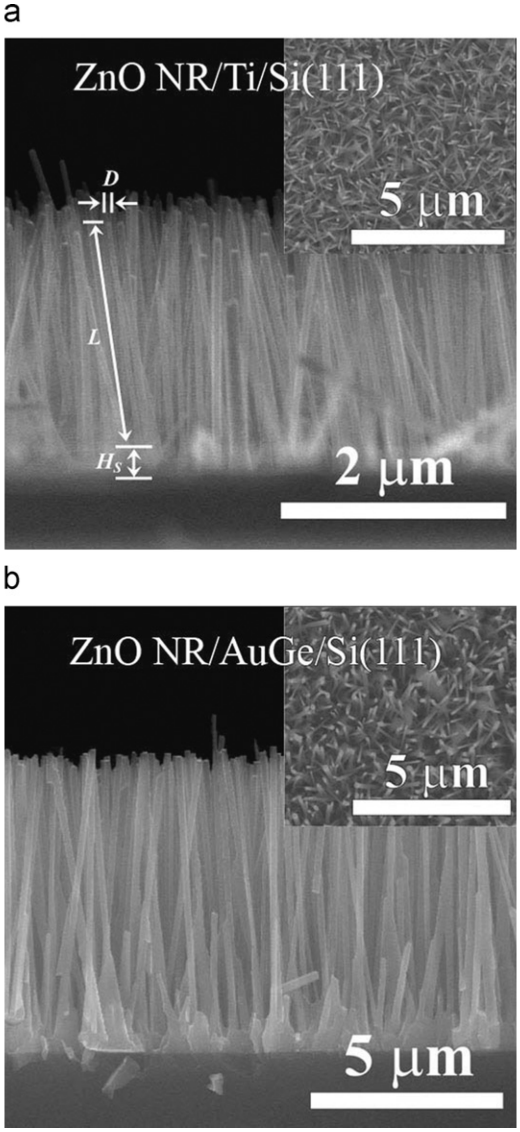

Fig. 2. Cross-sectional SEM images of ZnO NRs on various catalysts, the insets are plain-view images of (a) ZnO NRs/Ti/Si(1 1 1) and (b) ZnO NRs/AuGe/Si(1 1 1).

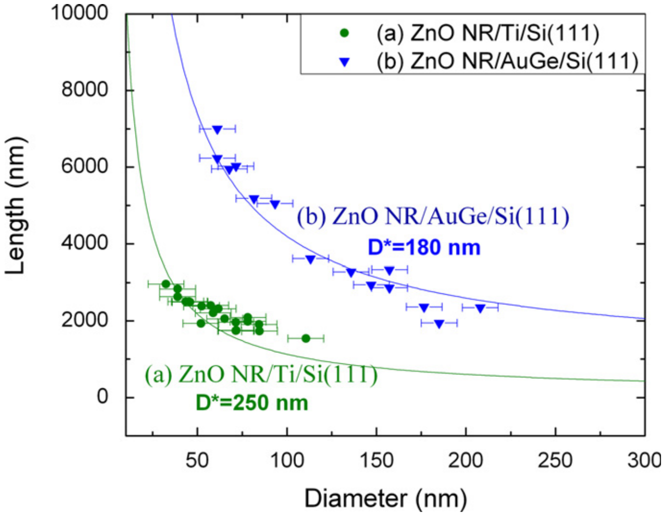

Fig. 3. Experimental and theoretical L–D dependencies for (a) ZnO NRs on Ti/Si(1 1 1) and (b) ZnO NRs on AuGe/Si(1 1 1). The theoretical curves (solid lines) were obtained using Eq. (2).