

In situ growth kinetics of ZnO nanobelts

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Abstract

For the first time, the growth of ZnO nanobelts was monitored *in situ* using x-ray diffraction. The growth was carried out by heating metallic zinc powder in air at temperatures ranging from 368 to 568 °C. The morphology depends on both the growth temperature and the rate of heating to that temperature. A morphology diagram for the synthesized products was generated after systematic study of the experimental parameters. Higher temperatures and faster heating rates favor one-dimensional growth. Faster growth was observed for samples with higher growth temperatures, lower heating rates, and one-dimensional growth. These results give insight into the mechanism for the growth of ZnO nanobelts by metal oxidation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Quasi-one-dimensional (1D) nanostructures of ZnO, with large aspect ratios and dimensions on the order of nanometers, have many potential applications as, for example, photonics materials [1], chemical sensors [2] and nanogenerators [3–5]. The nanowires are generally synthesized by a catalyst-mediated process involving vaporization of ZnO at high temperatures (around 950 °C). In most of the cases reported, the synthesis was carried out first, and the structure analysis was then performed post-mortem. As a result, detailed *in situ* structural monitoring was missed, leaving the question of growth kinetics unknown. Although there are some *in situ* transmission electron microscopy (TEM) observations of the growth of nanowires [6, 7], they are limited to a small number of nanowires, and lack statistical representation.

The objective of this paper is to monitor the growth of ZnO nanobelts/nanowires *in situ* by x-ray diffraction, aiming at understanding the growth kinetics. The synthesis of ZnO nanowires from metallic zinc at moderately low temperatures (around 500 °C) has previously been reported and attributed to a self-catalysis mechanism [8–11], in which metallic zinc serves both as source and catalyst, or to a tip-growth mechanism [12], in which Zn atoms diffuse through the ZnO nanostructure. Similar synthesis techniques have been applied to other oxides, such as MgO [13] and GeO₂ [11]. Some studies require molten zinc (melting temperature around 420 °C) [9–11], but ZnO nanowire synthesis has

also been reported from solid zinc at temperatures down to 350 °C [8]. The absence of an external catalyst may make these nanowires ideal for electronic applications, due to the lack of contaminating elements.

2. Experimental method

For synthesis, the source material was zinc metal powder (99%), with particle sizes on the order of tens of microns. The zinc powder was placed on an alumina plate and heated isothermally in an Anton-Paar HTK1200 furnace, which was left open to the air. A range of growth temperatures, from 368 and 568 °C, was investigated. The furnace was heated up to the growth temperature at a heating rate of 25, 30 or 35 °C min⁻¹. The furnace was held at the growth temperature for 80 min, then turned off and cooled in air to room temperature. The furnace was attached to a Panalytical X'Pert Pro diffractometer with Cu K α radiation, a Göbel mirror and an X'celerator position sensitive detector. Diffraction patterns were collected at room temperature before and after heating, and every 5 min at the synthesis temperature. The scan range was chosen to be 30°–40° 2 θ , to encompass the (0002) and (10 $\bar{1}$ 0) reflections of zinc and the (10 $\bar{1}$ 0), (0002) and (10 $\bar{1}$ 1) reflections of ZnO. The integrated area under the ZnO reflections, normalized by dividing by the integrated area under the zinc reflections in the initial room-temperature scan, was used as a measure of the volume of ZnO for kinetics analysis. After synthesis, the samples were investigated using a LEO field emission scanning electron microscope (SEM) and a JEOL 4000EX high-resolution transmission electron microscope (HRTEM).

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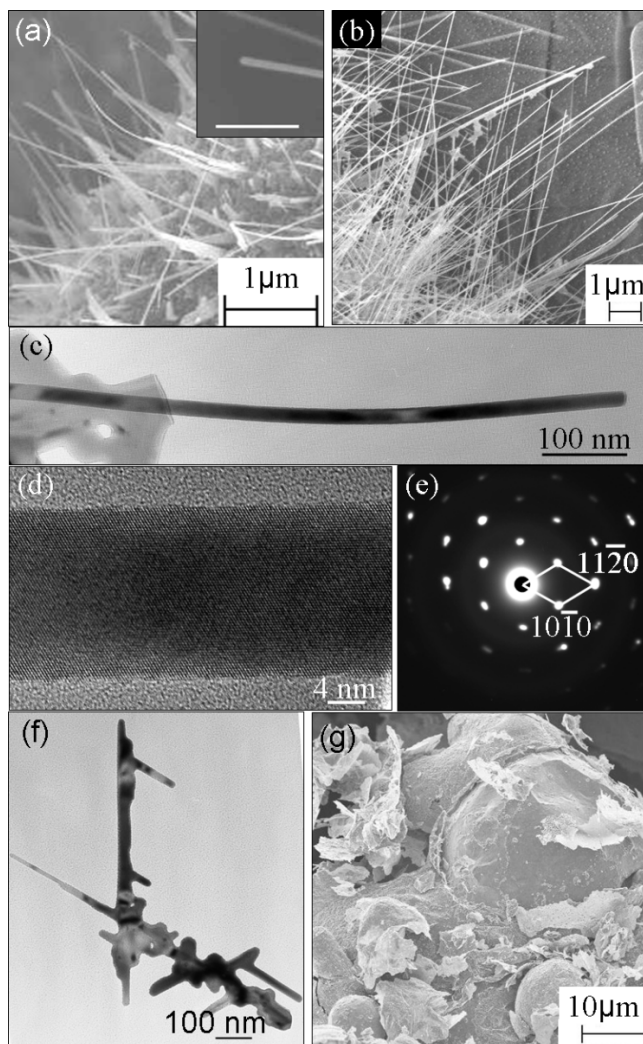


Figure 1. Electron microscopy of nanobelts, including (a) SEM images of nanobelts and nanofins grown for 80 min at 568 °C with a 25 °C min⁻¹ heating rate (inset scale bar 300 nm); (b) SEM image of longer nanobelts grown for 8 h at 518 °C with a 30 °C min⁻¹ heating rate; (c) TEM image, (d) HRTEM image and (e) electron diffraction pattern of a nanobelt grown for 80 min at 468 °C with a 35 °C min⁻¹ heating rate; (f) branched nanostructure grown for 80 min at 468 °C with a 35 °C min⁻¹ heating rate; (g) two-dimensional structures grown for 80 min at 518 °C with a 25 °C min⁻¹ heating rate.

3. Results and discussion

3.1. Growth morphology

The morphology of the nanostructures was investigated via scanning electron microscopy (SEM). Two classes are observed: one-dimensional and two-dimensional growth. For the samples exhibiting one-dimensional growth, several morphologies are observed, including nanowires, nanofins and branched nanostructures. The nanobelts grow out from the original zinc particles, having diameters around 20–30 nm and lengths of a few microns, with no catalyst particles at the tips, as seen in the inset in figure 1(a). Nanofins are usually observed intermingled with nanobelts. These structures are flat and are wider at the base, narrowing in steps to the tip, as in figure 1(a). The nanobelt length depends on growth time. In a

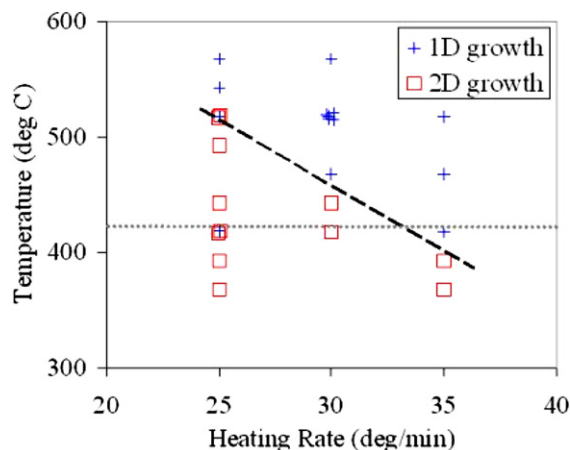


Figure 2. Morphology diagram illustrating dependence of morphology on temperature and heating rate. The dashed line separates the regions of 1D and 2D growth. The dotted horizontal line indicates the melting temperature of zinc.

sample grown for 8 h, the nanobelts are around 10 μm long, as seen in figure 1(b), and nanofins are less common.

Branched nanostructures are present in several samples. The branching exhibits hexagonal symmetry, reflecting the hexagonal crystal structure of ZnO, and occurs in one plane containing the main nanobelt, as seen in figure 1(f). Again, no catalyst particles are seen on the tips. Among samples exhibiting one-dimensional growth, higher growth temperatures favor straight nanobelts and fins, while lower temperatures favor branched nanostructures. High-resolution TEM (HRTEM) analysis of nanobelts, nanofins and branched nanostructures indicates that the nanostructures are single crystalline and that the growth direction is $\langle 11\bar{2}0 \rangle$, as shown in figure 1, which is consistent with the hexagonal symmetry of the branched nanostructures. The existence of branched nanostructures and split nanofins indicates that growth occurs at the tip of the nanostructure, not the base, ruling out the self-catalysis mechanism, in which growth occurs at the zinc/ZnO interface.

Other samples contain instead two-dimensional growth of ZnO layers on the original zinc particles. The existence of one-dimensional or two-dimensional growth depends on both the growth temperature and the heating rate, which will be discussed further in section 3.2 below. In samples with two-dimensional growth that were heated above 400 °C, the two-dimensional growth layers are seen to be peeling away from the particles, as in figure 1(g). When cooling from the growth temperature, a mismatch in the thermal contraction may cause the ZnO layers to detach from the zinc particles, as the linear thermal expansion coefficient of zinc is about four times that of ZnO.

3.2. Morphology diagram

As mentioned above, the growth morphology is affected by the growth temperature and the heating rate to that temperature. A morphology diagram, seen in figure 2, was constructed to illustrate the dependence of morphology on

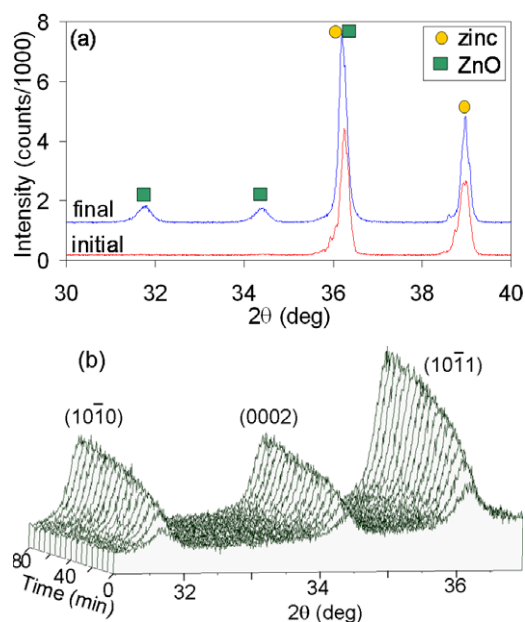


Figure 3. XRD scans collected (a) at room temperature before and after growth and (b) at 500 °C in 5 min intervals during growth. The heating rate is 30 °C min⁻¹.

temperature and heating rate. Faster heating rates and higher temperatures favor one-dimensional growth. (One anomaly was observed when heating up to 418 °C at 25 °C min⁻¹, where one sample exhibited one-dimensional growth, although all others exhibited two-dimensional growth.) The dependence of morphology on temperature may relate to the increase in the vapor pressure of zinc with temperature. A higher partial pressure of zinc around the particles may encourage one-dimensional growth, by increasing the availability of Zn away from the surface.

The reason for the dependence of morphology on the heating rate is less clear. The fact that changing the heating rate only changes the beginning of a synthesis run implies that its effect only occurs in the nucleation and perhaps initial growth stages. Another observation is that the growth mechanism does not require molten zinc, as a sample synthesized at 418 °C, with a heating rate of 35 °C min⁻¹, exhibited one-dimensional growth. The solid state of the zinc is evident by the presence of crystalline zinc reflections at the growth temperature. This is consistent with a previous study that found ZnO nanobelt growth from zinc at 350 and 400 °C [8].

3.3. Kinetics

The kinetics of the reaction were investigated via *in situ* x-ray diffraction data collected at the growth temperature. Initial scans for all samples contain zinc, with no ZnO present. Scans collected at 368 °C contain no significant ZnO signal, only zinc, indicating the absence of significant growth of ZnO, as in figure 3(a). Scans collected at 393–418 °C contain both ZnO and zinc reflections. Scans collected at temperatures of 443 °C and above contain only ZnO reflections, as the zinc is not crystalline. Despite the presence of molten zinc, SEM images show that the particles do not coalesce, indicating the presence of a ZnO shell that is able to contain the molten zinc,

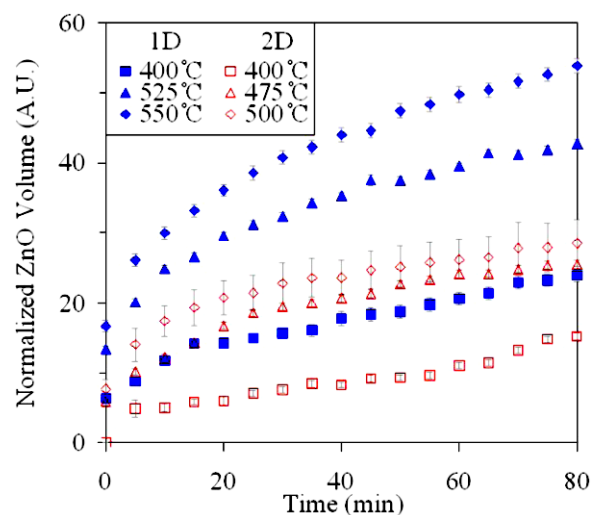


Figure 4. Normalized ZnO volume versus time for samples heated at 25 °C min⁻¹ to different temperatures resulting in one- or two-dimensional growth.

which is consistent with prior studies of zinc oxidation [14, 15]. For each sample where ZnO grows, the strength of the ZnO reflections grows with time, as seen in figure 3(b). The growth is initially quick, gradually slowing down.

Figure 4 displays the normalized ZnO volume curves for samples with a 25 °C min⁻¹ heating rate at different temperatures and with different morphologies. Data for samples with other heating rates, though not presented, exhibit the same trends. Generally, the curves do not begin at the origin, indicating that growth initiates before reaching the growth temperature. For samples having the same heating rate and the same dimensionality of growth, higher temperatures yield faster kinetics. This is not surprising, since higher growth temperatures will lead to higher zinc vapor partial pressures and faster Zn diffusion. Samples exhibiting one-dimensional growth have faster kinetics than those exhibiting two-dimensional growth. In the case of two-dimensional growth, the formation of thicker ZnO layers on the zinc particles may limit the vaporization or inhibit the diffusion of zinc, leading to slower kinetics. X-ray data will, of course, sample ZnO layers on the zinc particle surface in addition to ZnO nanostructures. The consistent trend in the effect of the growth morphology on the kinetics supports that the signal from ZnO nanostructures is not being overshadowed by the signal from ZnO layers.

Finally, for samples with one-dimensional growth, faster heating rates give slower kinetics at the same growth temperature, as illustrated in figure 5, which displays the normalized ZnO volume curves for samples exhibiting one-dimensional growth at different temperatures and heating rates. (The data for the relationship between heating rate and kinetics for samples with two-dimensional growth are inconclusive.) The effect of the heating rate on both the morphology and kinetics suggests that the nucleation and initial growth stages are vital in controlling the growth of ZnO nanostructures. Similar trends are likely to occur in the growth of oxide nanostructures from other metals that have similar interactions with oxygen.

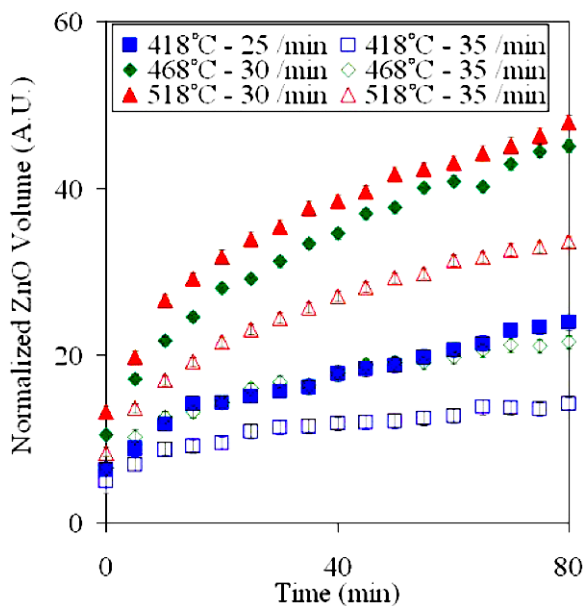


Figure 5. Normalized ZnO volume versus time for samples exhibiting one-dimensional growth with different temperatures and heating rates.

4. Summary

In summary, the results discussed above provide some clues about the mechanism for the synthesis of ZnO nanobelts by heating zinc in air. The zinc particles are covered by a ZnO layer [14, 15], which is subjected to thermal stresses when heating, due to differences in the thermal expansion of zinc and ZnO. The ZnO layer may crack from these stresses, exposing metallic zinc, where it can react with O₂ in the atmosphere and either transport to existing nuclei on the skin or form new nuclei for the growth of ZnO nanobelts. The finding that faster heating rates promote one-dimensional growth indicates that this first step is vital in determining the morphology. The nuclei may be susceptible to dissolution at elevated temperatures. Faster heating rates mean less time before growth at elevated temperatures, leading to a smaller probability that the nuclei will dissolve before growth. The faster heating rate will

also produce more stress fractures in the ZnO skin releasing more Zn for vaporization. The dependence of morphology on heating rate may also explain the disagreement in previous studies, some of which found that nanobelt growth requires molten zinc [9–11], while others synthesized ZnO nanobelts below the zinc melting temperature [8]. It is apparent that more synthesis parameters than just growth temperature must be considered in order to control the growth of nanobelts via metal oxidation.

Acknowledgment

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