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Synthesis of vertically aligned ultra-long ZnO nanowires on heterogeneous substrates with catalyst at the root

Guang Zhu[1], Yusheng Zhou[1], Sihong Wang[1], Rusen Yang[2], Yong Ding[1], Xue Wang[1,3], Yoshio Bando[4] and Zhong lin Wang[1]

[1] School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA
[2] Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, USA
[3] Department of Applied Physics, Chongqing University, Chongqing 400044, People's Republic of China
[4] World Premier International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science, Namiki1-1, Tsukuba, Ibaraki 305-004, Japan

E-mail: zlwang@gatech.edu

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Abstract

The synthesis of ultra-long high-quality ZnO nanowires with uniform size and orientation on heterogeneous substrates is highly desirable, not only for investigating the fundamental properties of ZnO nanowires, but also for fabricating integrated functional nanodevices. Here we present a novel and general technique for growing vertically aligned ultra-long ZnO nanowires on various substrates. More importantly, the metal catalyst is experimentally determined not at the tip ends of the nanowires but at the junction area between the nanowires and the underlying substrate. Based on detailed analysis and control group results, we then propose a three-stage growth mechanism, in which vapor–liquid–solid growth and vapor–solid growth compete with each other to become dominant.

(Some figures may appear in colour only in the online journal)

1. Introduction

In the last decade, one-dimensional (1D) ZnO nanostructures, such as nanowires (NWs), nanobelts, and nanorods have been receiving considerable attention due to their unique properties for electronic and optoelectronic applications [1–4]. A variety of ZnO NW based devices have been demonstrated, including field effect transistors [5–7], UV lasers [8, 9], light emitting diodes [10–12], solar cells [13–15], photodetectors [16–18], nanogenerators [19–21], and piezotronics [22, 23]. As the basis for various applications, synthesis with control over size, orientation, and density is of great significance and very much desired. The main synthesis techniques include physical vapor deposition [1, 5, 24, 25], chemical vapor deposition [26–29], pulsed layer deposition [30] and the wet chemical method [31–33]. For the widely employed vapor transport method, different growth mechanisms have been reported, including catalyst-assisted vapor–liquid–solid (VLS) growth and catalyst-free vapor–solid (VS) growth. On one hand, the VLS mechanism usually yields ZnO NWs with size and orientation uniformity, but residual metal catalyst particles often stay at the tips of the NWs [34], which is very detrimental to further device integration because these particles prevent intimate contact between the NWs and electrode materials. Besides, as demonstrated by previous reports, the lengths of the ZnO NWs grown from the VLS mechanism are limited to only a few micrometers [26–28]. On the other hand, methods with the VS mechanism can grow ZnO NWs with lengths up to hundreds of micrometers, which nevertheless generally have rather poor alignment and uniformity [1, 35].

Here we report a uniquely modified and general technique of synthesizing ultra-long ZnO NWs with great vertical alignment on different substrates, with length and aspect ratio exceeding 130 μm and 500, respectively. More importantly, pre-deposited metal catalysts were experimentally confirmed

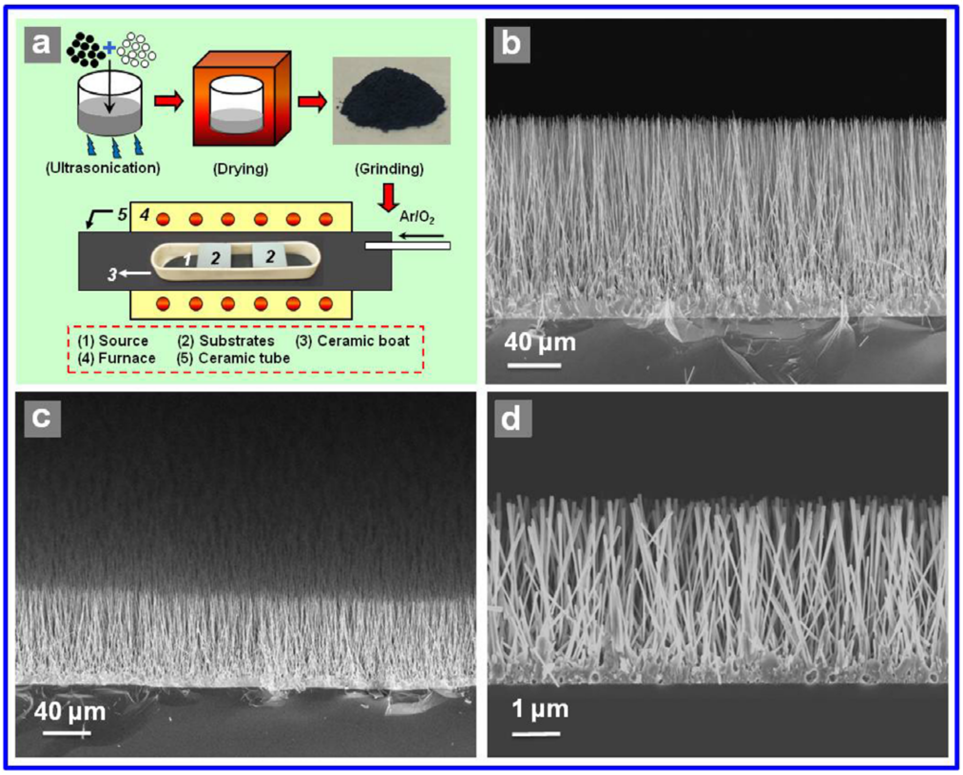

Figure 1. (a) Schematic illustration of the source material preparation and the horizontal furnace system for the synthesis of ultra-long ZnO NW arrays. (b) Cross-sectional view of the synthesized ZnO NWs on the Si substrate. (c) 60° tilted view of the synthesized ZnO NWs on the Si substrate. (d) Cross-sectional view of the synthesized ZnO NWs using conventional source materials without pretreatments.

at the roots instead of the tip ends of the NWs. Furthermore, a series of control experiments was conducted to investigate the actual growth mechanism. Finally, a unique growth model was proposed, combining VLS and VS growth in three consecutive stages. Our synthesis technique opens up the path for fabricating various functional devices based on high-quality ZnO NW arrays.

2. Experimental section

In general, the limited length of NWs synthesized by the chemical vapor transport method is possibly due to the relatively low reactive vapor concentration in the synthesis tube and thus the slow growth speed. To overcome this challenge, two unique strategies were employed in our work. The first one involves pretreatment of the source materials, as schematically illustrated in figure 1(a). Rather than using the conventionally used ZnO powder and graphite powder, we used commercially available ZnO nanopowder (Sigma-Aldrich) and activated carbon powder (Alfa Aesar) as source materials. Respectively, amounts of 1 g were used as received. They were then dispersed in ethanol. The suspension was ultrasonicated for 30 min to ensure uniform dispersion. Then it was put in a hot oven for drying for another 30 min. After the ethanol had completely vaporized, the dried mixture was then well ground and ready for use. The use of nano-sized source materials and the pretreatment measures are expected to greatly increase the amount of reactive vapor released during the growth. The second strategy was to modify the conventional synthesis configuration in which the source materials and substrates are separately located at the center and downstream side of the furnace tube, respectively. As shown at the bottom of figure 1(a), the already prepared source materials were transferred to an alumina boat. Silicon wafer substrates coated with gold thin film were horizontally mounted on top of the boat with the gold layer facing down. This non-conventional configuration is expected to greatly increase the local concentration of the reactive vapor at the growth site and the growth speed as a result [36]. The boat was then placed at the center of the furnace tube. Silicon wafer (100) substrates were dipped in buffered oxide etching (BOE) solution for 10 s to strip off the native oxide layer, cut into 1.8 cm × 1.8 cm pieces and then rinsed by acetone, methanol, and isopropyl alcohol, consecutively. A 2 nm gold catalyst layer was coated by e-beam evaporation with a deposition rate of 0.1 Å s^{-1}. During the growth, the temperature was ramped up to 960 °C at a rate of 60 °C min^{-1} with a constant flow of carrier gas (30 sccm of argon and 10 sccm of oxygen). The reaction lasted for 30 min. After the reaction, the furnace was cooled down to ambient temperature for product collection.

The morphology of the synthesized ZnO nanowires was examined by an LEO 1530 SEM at 5 kV accelerating voltage. The XRD data were collected with Cu Kα radiation on a Panalytical X'Pert PRO Alpha-1. The TEM image of a single ZnO nanowire was recorded on a Hitachi HF-2000 with an accelerating voltage of 200 kV. The TEM images of

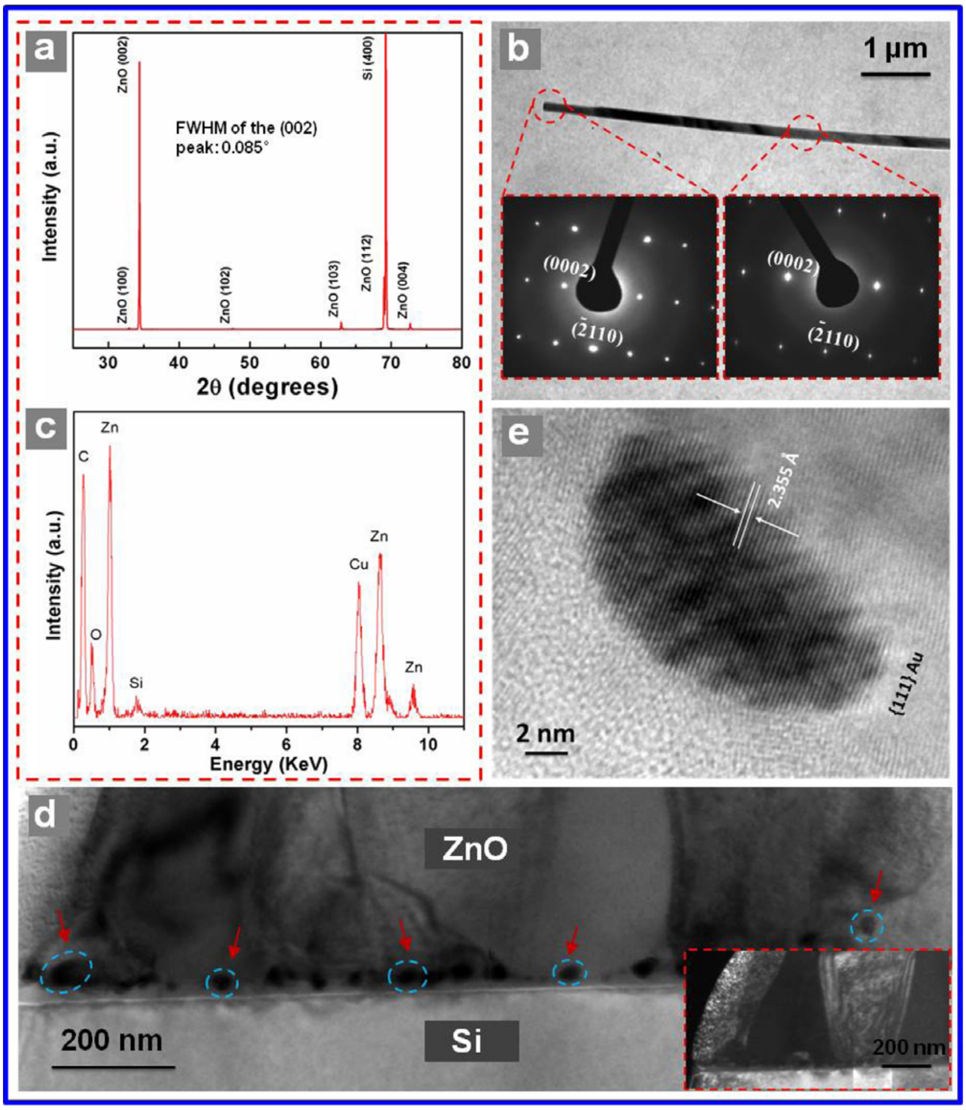

Figure 2. Detailed characterization results of the synthesized ZnO NWs. (a) X-ray diffraction patterns of the as-grown vertical aligned ZnO NWs on Si(100). (b) TEM image of a single ZnO NW. The insets are selected-area electron diffraction patterns at the tip (left) and the body (right). (c) Energy dispersive spectrum acquired at the tip of the NW. (d) TEM image at the interface area between the grown ZnO crystal and the substrate, with catalyst particles highlighted by circles and arrows. The inset is the dark field TEM image of the interfacial area. (e) HRTEM image of a single catalyst particle, revealing the {111} surface of gold crystal.

the NW/substrate interfacial area were acquired by a JEOL 4000EX at 400 kV accelerating voltage.

In the control experiments, which were designed to justify the proposed model, the ZnO and ITO thin film were deposited by a PVD75 RF sputterer with a thickness of around 100 nm. The SiO_2 substrate was prepared on a Si wafer by thermally growing an oxide layer of 200 nm by a Lindberg furnace.

3. Results and discussion

The synthesized ZnO NWs are extremely long with lengths of up to 130 μm (figure 1(b)). They are very well aligned at vertical orientation and densely packed with great size uniformity (figure 1(c)). For the purpose of comparison, we also grew NWs using as-received commercial ZnO powder and graphite as source materials without the described pretreatment, which yielded only NWs of a few micrometers in length with lower density and more random orientations (figure 1(d)). It is noteworthy that there is a ZnO crystal film at the junction between the NWs and the substrate. Reports concerning this so called buffer layer or seed layer have been published. Some researchers believe that this layer is deposited on the substrate first and then subsequent nucleation and growth of the NWs follow [24, 37]. But some others believe that it is the convergence of the densely packed adjacent NWs that leads to the formation of a continuous film. However, the origin of such a layer still remains controversial [25].

The crystal structure of the NWs was characterized by x-ray diffraction (XRD) and transmission electron microscope (TEM) (see section 2 for details). The XRD patterns reveal that the synthesized NWs are single crystalline ZnO (figure 2(a)). Apparently, a strong (002) peak is

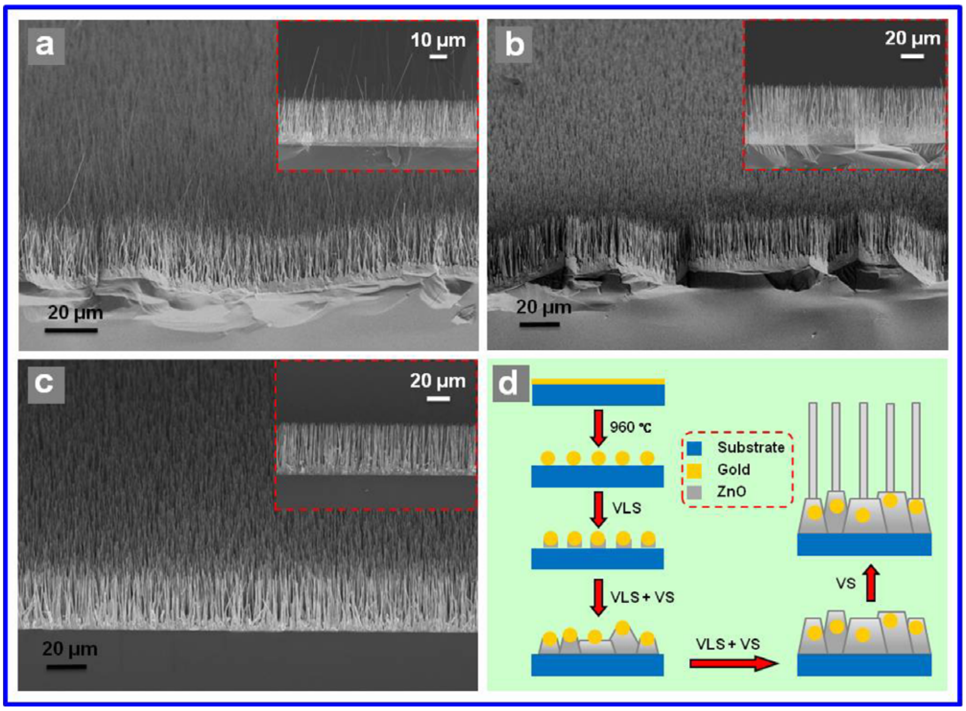

Figure 3. (a) 60° tilted view of the synthesis result on a ZnO substrate, with no catalyst applied before growth. The inset is the cross-sectional view. (b) 60° tilted view of the synthesis result on an ITO substrate, with catalyst applied before growth. (c) 60° tilted view of the synthesis result on a SiO_2 substrate, with catalyst applied before growth. (d) Schematic illustration of the ZnO NW growth process via a three-stage mechanism.

overwhelmingly predominant with other peaks almost negligible, indicating uniform orientation as well as great density of the NWs. A TEM image of a single NW (figure 2(b)) shows a typical diameter of 250 nm. The selected-area electron diffraction (SAED) pattern proves again the single crystalline nature of the NW and exhibits the growth along the [0001] direction (right inset of figure 2(b)). It is observed from the TEM image that the NW tip seems to be free of any catalyst particle! The SAED pattern acquired at the tip shows no patterns other than ZnO crystal (left inset of figure 2(b)). Besides, the EDS spectrum measured at the tip also gives no trace of gold element (figure 2(c)), confirming that the gold catalysts are absent from the tip end.

Although the observation that catalyst-assisted growth produces NWs with catalyst-free tip ends has been reported [19, 20, 36, 38–40], very few successful attempts have been made to determine the underlying reason. Some researchers believe that the catalyst is doped into the NW as contamination [24], while some others suggest that it evaporates during the growth process [19, 20]. However, convincing experimental results are lacking. Here, we prepared extremely thin cross-sectional samples for TEM characterization. The TEM image targeting the NW/substrate interfacial area reveals a very interesting phenomenon. A layer of particles can be clearly spotted at the roots of the NWs, which is highlighted in figure 2(d). The dark field TEM image (inset of figure 2(d)) reveals the continuous ZnO film lying between the NWs and the substrate to be a textured layer, which is composed of adjacent crystal domains. The high resolution transmission diffraction (HRTEM) image of a single particle exhibits a set of lattice planes with a measured distance of 2.35 Å, corresponding to {111} of gold crystal. The decisive experimental evidence confirms that the metal catalyst stays at the roots of the synthesized ZnO NWs. This phenomenon is a strong indication that the ZnO NW synthesis using our technique is not simply governed by the VLS mechanism, which is consistent with a previous report by Fan *et al* [38]. It is noticeable that the catalyst particles do not adhere closely to the underlying substrate and that their respective distances away from the substrate vary. As a result, they are expected to have negligible influence on the electron transport behavior at the NW/substrate interface.

Such an unexpected discovery raises two important questions, i.e. how the metal catalyst ends up staying at the interfacial area and what role it plays during the growth process. To shed light on the actual growth mechanism, a series of control experiments was performed.

In the first group, no gold catalyst was pre-deposited on the substrate, while the other experimental parameters remained unchanged. As a result, NW growth was not observed, which is a strong proof that the gold catalyst is indispensable for initializing the growth [36, 40].

In the second group, a sputtered ZnO film as a seed layer was prepared on a bare Si substrate surface, and no catalyst was applied. The growth result is presented in figure 3(a). Vertically oriented ZnO NWs with a length of tens of micrometers were successfully synthesized, indicating that VS growth should be dominating if a seed layer is provided [24, 25, 37].

In the third group, a ITO film was sputtered on a Si bare substrate surface, followed by coating a gold catalyst layer. Ultra-long ZnO NW arrays were synthesized with high quality, as shown in figure 3(b). Other substrates, such as thermally grown SiO_2, yielded similar results (figure 3(c)). This is a strong indication that the growth is truly catalyst-assisted. As long as the gold catalyst is provided, the growth can take place no matter what the underlying substrate is. In addition, this observation proves that our synthesis technique is very general, and is applicable to other substrates besides Si wafer. Therefore, various heterojunctions are expected to be formed.

Based on our characterization analysis and control groups, we propose a three-stage growth model, as schematically illustrated in figure 3(d). During the growth, Zn vapor is generated by carbon thermal reaction [26]

$$\mathrm{ZnO\ (s) + C\ (s) \longleftrightarrow Zn\ (v) + CO\ (v)} \tag{1}$$

followed by [28]

$$\mathrm{2Zn\ (v) + O_2\ (v) = 2ZnO\ (v).} \tag{2}$$

Between the Zn vapor and ZnO vapor, which one would participate in the NW growth depends on the surface condition of the substrate.

In the early stage of the growth, it is the Zn vapor that can be easily dissolved into the gold particles to form liquid alloys. Upon supersaturation, it reacts with oxygen, precipitating out very thin ZnO textured seeds beneath the catalyst particles [26]. Thus the first stage is purely dominated by VLS growth.

Then the seeds provide nucleation and growth sites for ZnO vapor [24, 38]. The abundant and continuous arrival of ZnO vapor makes very rapid VS growth possible [35], which may far exceed the VLS growth. Consequently, the catalyst particles will soon be submerged because of the VS growth, which can explain why the catalyst particles do not adhere to the undying substrate but are encapsulated by ZnO crystal. Therefore, in the second stage, although VLS growth does not cease, it is the VS growth that prevails.

In the last stage, the catalyst particles have been isolated from the reagent vapor and do not play any role afterward. As a result, only the VS mechanism contributes to the further growth of ZnO NWs [24]. Therefore, based on our model, the metal catalyst mainly plays two roles. First, it is crucial for initializing the growth by absorbing Zn vapor. Second, it precipitates ZnO texture seeds, which not only provide templates for further growth but also guide the growth orientation, leading to alignment of the NWs.

4. Conclusions

In summary, we developed a uniquely modified and general technique for synthesizing vertically aligned ultra-long ZnO NWs on various substrates. The NWs have great density and uniformity, with length and aspect ratio exceeding 130 μm and 500, respectively. Catalyst particles were experimentally proved to be at the NW/substrate interface area instead of the tip ends. A series of control experiments was performed to understand the growth process. A three-stage growth model was then proposed. It involves a combination of VLS growth and VS growth, which compete with each other to become dominant. Our technique opens up a path for fabricating integrated high-performance devices based on ZnO NW arrays.

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