

Growth of Vertically Aligned ZnO Nanobelt Arrays on GaN Substrate

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Uniformly aligned ZnO nanobelt (NB) arrays have been grown on a (0001) GaN substrate without foreign catalyst such as Au. The NBs mainly grew along [01 $\bar{1}$ 3] at beginning when the temperature was relatively low, then switched to [01 $\bar{1}$ 0] at high temperature, and finally switched to [01 $\bar{1}$ 3] when the temperature was lowered. The alignment of the NBs was due to not only the epitaxial orientation relationship with the substrate but more importantly the presence of metallic Zn nanoparticles at the tip of the ZnO NBs, which were produced by reduction of ZnO source material. The Zn nanoparticle has a fixed orientation relationship with the ZnO NB, indicating that the growth follows the self-catalyzed vapor–liquid–solid process.

Recently, one-dimensional (1D) ZnO nanostructures, such as nanobelts (NBs)¹ and nanowires,² have attracted a great research attention for applications in sensors,³ light emitting diode,⁴ field emission,⁵ power generation,⁶ solar cell,⁷ and piezotronics.⁸ In the family of NBs, ZnO is probably the most extensively studied structure. Compared with nanowires, NBs have a rectangular cross-section with well defined crystallographic surfaces. This type of geometrical shape makes NBs unique for applications such as cantilevers⁹ and lateral devices on substrate.¹⁰

Much effort has been devoted to growing vertically aligned ZnO nanowires using Au nanoparticles as catalyst.^{2,11} The nanowires typically have a hexagonal shape with growth direction along [0001] and their side surfaces are enclosed by {1 $\bar{1}$ 00} or {2 $\bar{1}$ $\bar{1}$ 0} facets. This is the most easy growth configuration of ZnO nanowires. However, there are few reports about the growth of aligned oxide NBs.^{5,12}

In this paper, we demonstrate the synthesis of vertically well-aligned NB arrays on a GaN substrate. The growth of the uniform aligned NBs is produced by a vapor–solid decomposition process without using any foreign catalyst. After analyzing the structure of the NBs, a growth mechanism is proposed to understand their formation process.

The ZnO NBs were synthesized by a solid–vapor process.¹³ ZnO powder (3 g) was loaded in an alumina boat that was positioned in the middle of an alumina tube. A 2 μm thick, *c*-plane oriented GaN thin film grown on an *a*-plane sapphire wafer was used as the substrate, which was placed down stream from the source material with GaN surface facing downward in the alumina boat. The tube was then placed in a horizontal tube furnace, in which the source material was located at the highest temperature zone. The deposition system was pumped down to ~ 20 mTorr overnight to remove the residual oxygen

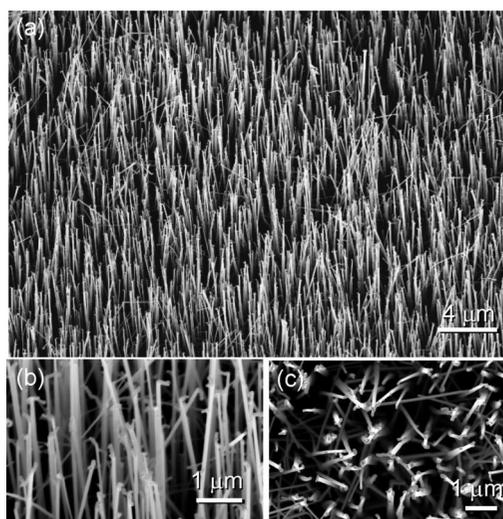


Figure 1. SEM images of vertically well-aligned ZnO nanobelt arrays grown on GaN substrate. (a, b) Low- and high-magnification 30° side view SEM images of the grown nanobelt array, respectively. (c) High-magnification top view SEM image of the grown nanobelt array.

and water. Then the source materials were heated to 1475 °C at a heating rate of 50 °C/min. Argon carrier gas was introduced at a flow rate of 50 sccm (standard cubic centimeters per minute) when the temperature reached 300 °C. The source material was heated at 1475 °C for 60 min. The NBs were deposited onto an alumina substrate placed in a temperature zone of 500–600 °C under a pressure of 23 Torr. Then the furnace was turned off, and the tube was cooled naturally down to room temperature under an argon flow.

The as-synthesized ZnO NBs were first characterized by scanning electron microscopy (SEM, JEOL LEO1550). The ZnO NBs were deposited on both sides of the substrate. The top surface was unpolished sapphire, where randomly oriented and long ZnO NBs were formed. Interestingly, as shown in Figure 1a, the vertically well-aligned ZnO NBs were grown at the bottom surface of the substrate, where a *c*-plane oriented GaN thin film was coated. The widths of the NBs grown on the GaN

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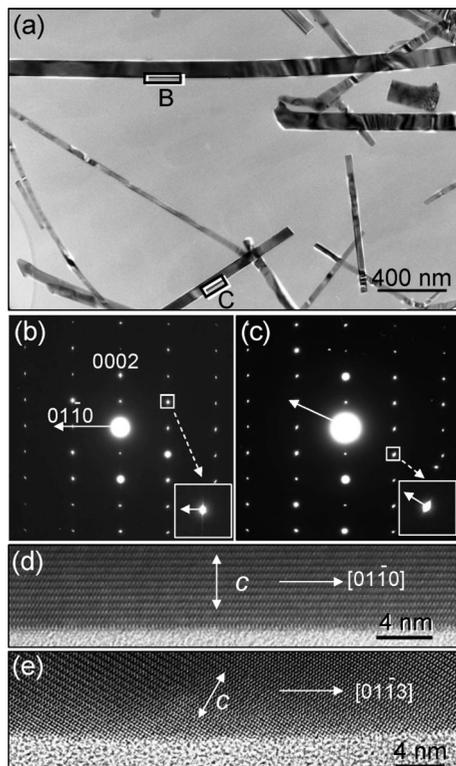


Figure 2. (a) Low-magnification TEM image of ZnO nanobelts. (b and c) SAED patterns taken from rectangles B and C areas in (a), respectively. (d and e) High-resolution TEM image of nanobelts B and C, which are grow along $[01\bar{1}0]$ and $[01\bar{1}3]$, respectively. Note the relative rotation of the diffraction patterns in reference to the image was not adjusted for nice display purpose.

range from 40 to 200 nm and their lengths are $\sim 5 \mu\text{m}$. Higher magnification side view and top view SEM images are shown in Figure 1b,c, respectively. It clearly shows the growth direction change close to the tips of NBs. Also there is a particle located at the tip of each NB, which can be seen more clearly in the transmission electron microscopy (TEM) images. The presence of the Zn particle at the tip indicates a growth process by self-catalyzed vapor–liquid–solid (VLS) process, because the Zn nanoparticles were produced by the decomposition of ZnO powder. We will discuss it in detail after the growth direction identification using TEM.

More structural characterizations of the ZnO NBs were carried out using TEM (JEOL 4000EX). Figure 2a shows an enlarged TEM image of several individual ZnO NBs. Each NB is uniform in width along the growth direction, and the bending contour indicates the same thickness across the belt. Select-area electron diffraction (SAED) patterns from the two rectangular areas labeled B and C are shown in Figure 2b,c, respectively. Both SAED patterns are with electron beam along $[2\bar{1}\bar{1}0]$. Due to the quasi-one-dimensional morphology, the growth directions of each NB can be identified based on the shape effect in diffraction spots. The insets in Figure 2b,c give the enlarged diffraction spots, from which we can identify the streaking directions, which are perpendicular to the growth direction of the NB. The growth direction of the NB at the top of Figure 2a is along $[01\bar{1}0]$, while the growth front of the bottom NB is $(01\bar{1}1)$ plane with growth direction as $[01\bar{1}3]$. The growth directions of these two NBs can be further confirmed by their high-resolution TEM (HRTEM) images displayed in Figure 2d,e respectively. Among more than 20 NBs we have examined, 90% of them take either $[01\bar{1}0]$ or $[01\bar{1}3]$ as their growth directions.

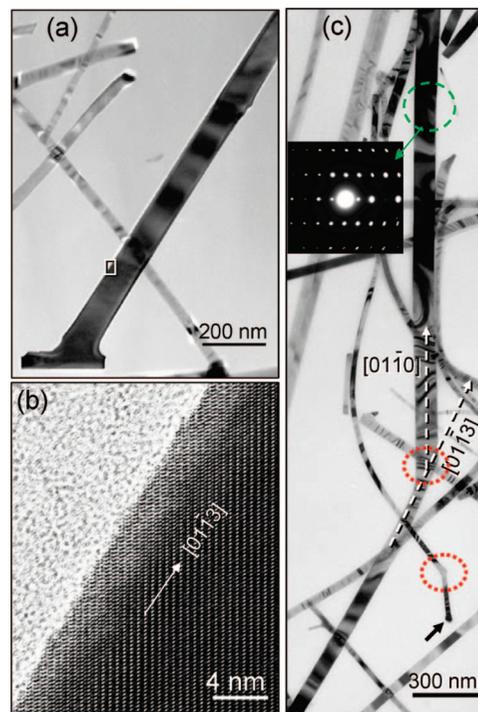


Figure 3. (a) Low-magnification TEM image of the root of a ZnO nanobelt in contact with the GaN substrate. (b) High-resolution TEM image from the rectangular area in (a). The root of the nanobelt grows along $[01\bar{1}3]$ direction. (c) TEM image shows the turning point (circled area) of the growth direction from $[01\bar{1}3]$ to $[01\bar{1}0]$. Inset: the SAED pattern of the largest nanobelt shown in (c).

$[01\bar{1}0]$ is one of the most common NB growth directions, while $[01\bar{1}3]$ NB is quite rare.

Each belt we examined using TEM is only part of the whole nanostructure grown from the substrate. Different sections of NBs can be distinguished upon their morphologies. During the vapor deposition process, a seed layer was first epitaxially grown on the substrate, then ZnO NBs grew up from such a thin film layer. So the belt in Figure 3a looks peeled off from a thin film layer, which is in fact the root of the NB binding with the GaN substrate. Figure 3b is a high-resolution TEM image of the rectangle area in Figure 3a. The growth direction can be uniquely identified as $[01\bar{1}3]$, which is the starting growth direction. In Figure 3c, an arrowhead points to a particle at the growth front of the NB. The uniform contrast of the NB and the inserted SAED pattern indicate that it is a single crystal with two growth directions along $[01\bar{1}0]$ and $[01\bar{1}3]$, respectively. The turning points when the growth direction changed between $[01\bar{1}0]$ and $[01\bar{1}3]$ are circled in Figure 3c. One of them shows that the growth direction switched at the tip of the NB. Figure 4a confirms that the ZnO NB grew along $[01\bar{1}3]$ at the tip. From the analysis above, we can see that the NBs initially grew along $[01\bar{1}3]$, then switched to $[01\bar{1}0]$ during growth, and then the final part of the ZnO NBs took the $[01\bar{1}3]$ as its growth direction.

The change of growth direction is mainly effected by the temperature variation during the deposition process. Since the source materials were heated to $1475 \text{ }^\circ\text{C}$ at a rate of $50 \text{ }^\circ\text{C}/\text{min}$, such a temperature was significantly higher than the temperature used for growing $[0001]$ nanowires, which is typically $\sim 1000 \text{ }^\circ\text{C}$. During the growth, it took $\sim 30 \text{ min}$ before the furnace to reach the peak temperature. Argon was introduced at a flow rate of 50 sccm when temperature reached $300 \text{ }^\circ\text{C}$. The source material, ZnO powder, was decomposed before the

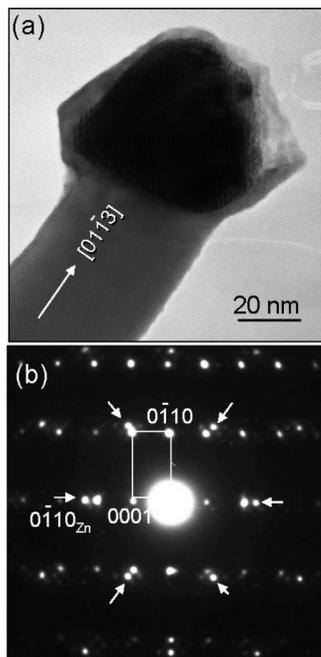


Figure 4. High-resolution TEM image (a) and corresponding SAED pattern (b) of a ZnO nanobelt with a Zn particle located at its tip. Note the relative rotation of the diffraction patterns in reference to the image was not adjusted for nice display purpose.

temperature was raised to 1475 °C. The NBs started growing along $[01\bar{1}3]$ at a relatively lower temperature. The growth direction switched to $[01\bar{1}0]$ when temperature was stabilized at the peak value. Once the furnace was turned off, the source material and substrate were slowly cooled down to room temperature under an argon flow. ZnO NBs took the $[01\bar{1}3]$ as growth direction again at lower temperature.

Both SEM and TEM images show nanoparticles at the tips of the NBs. The particle was examined by HRTEM and SAED. Figure 4a shows a single crystalline Zn particle that is covered by a thin ZnO layer, which was formed due to the oxidation of Zn when exposed to air. The particle's SAED pattern is displayed in Figure 4b, which is composed of two patterns; one is ZnO $[2\bar{1}\bar{1}0]$, and another one is the Zn $[0001]$ pattern as indicated by white arrowheads. The lattice match configuration can be described as $(2\bar{1}\bar{1}0)_{\text{ZnO}} \parallel (0001)_{\text{Zn}}$, $[0001]_{\text{ZnO}} \parallel [01\bar{1}0]_{\text{Zn}}$. The observation of Zn particle and its lattice match to ZnO NB indicates the existence of a self-catalyzed growth process. In our experiment the only source material was pure ZnO powder and there was no foreign catalyst deposited on the substrate. The Zn self-catalyzed growth of ZnO nanowires/NBs has been proposed previously.¹⁴ Our experiment gives the direct evidence of such self-catalyzed growth using ZnO decomposed Zn particle.

Without the presence of heterocatalysis particles, the growth of a uniform belt structure usually follows vapor–solid (VS) mechanism.¹ Here we proposed a self-catalyzed vapor–liquid–solid process to explain the growth of aligned ZnO NB arrays. The Zn came from the decomposition of ZnO. In our experi-

ment, the substrate was placed in a temperature zone of 500–600 °C, which is higher than the bulk melting point of Zn (419.53 °C). The Zn was in the liquid state during growth. The liquid Zn droplet was the favorable site for the adsorption of new Zn and O₂ species, resulting in the growth of ZnO NB. It is possible there are a few atomic layers of locally ordered Zn at the Zn–ZnO interface due to the coherent interfacial “pinning”¹⁵ owing to the high melting point of ZnO (1975 °C).¹⁶ The Zn droplet is locally crystallized or atomically ordered at the interfacial region with the ZnO to trigger the initial nucleation and subsequent growth of the NB so that the crystalline structure of the Zn determines the growth direction and subsequently the side surfaces of the NB. The Zn droplet turned to single crystal after the temperature was dropped, and its surface was oxidized to ZnO when exposed to air. There is another possibility that the growth direction was determined by substrate. The Zn particle was in the liquid state during growth, and it is crystallized after growth and matches the orientation of the NB.

In summary, for the first time, vertically well-aligned ZnO NB arrays were synthesized via vapor phase transport process. The Zn particle was observed at the tip of the NB, and a self-catalyzed vapor–liquid–solid growth mechanism was proposed about the growth of aligned NBs. The ZnO NB changed its growth directions between $[01\bar{1}0]$ and $[01\bar{1}3]$ during growth, which was suggested as a result of variation of growth temperature.

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