

# Homojunction of Single-Crystalline ZnO Nanowire/Nanowall Network on $c\text{-Al}_2\text{O}_3$ Substrate Formed by Thermal Vapor Phase Epitaxy Method

Sammook Kang, Tong Ik Shin, Sang-Woo Kim<sup>1</sup>, and Dae Ho Yoon<sup>2\*</sup>

School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 440-746, Korea

<sup>1</sup>School of Advanced Materials and System Engineering, Kumoh National Institute of Technology, Gumi, Gyeongbuk 730-701, Korea

<sup>2</sup>SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440-746, Korea

Received January 7, 2009; accepted June 1, 2009; published online September 24, 2009

Homojunctional ZnO nanowire/nanowall structures were synthesized using a vapor phase epitaxy method. The homojunctional ZnO nanowire/nanowall structures are vertically well aligned having a random honeycomb-like pattern, and the metal catalyst only exists on the ends of the ZnO nanowires. The ZnO nanowires and nanowall synthesized on  $c\text{-Al}_2\text{O}_3$  in the vapor–liquid–solid mode form a single unit and are part of the same single crystal. We focused on the study of the growth mechanism and crystal structure of homojunctional ZnO nanowire/nanowall structures. © 2009 The Japan Society of Applied Physics

DOI: 10.1143/JJAP.48.095502

## 1. Introduction

ZnO is a very interesting material for optical applications because of its wide band gap of 3.37 eV. A prominent feature of ZnO is its high exciton binding energy (60 meV) at room temperature, which leads to an extremely high stability of its excitons,<sup>1)</sup> and enables devices to function at a low threshold voltage. ZnO is promising for applications in blue light-emitting diodes (LEDs), field-effect transistors (FET), ultraviolet laser diodes (LD), sensors, acousto electrical devices, and detectors.<sup>2)</sup> In particular, nanostructured materials possess unique electric, optical, and magnetic properties compared with the corresponding bulk materials. This is due to the quantum confinement effect, Coulomb blockade effect, and high surface-to-volume ratio. Semiconductor nanowires can be produced using a nanoscale junction. The realization of nanoscale semiconductors depends on the ability to integrate these structures into functional devices, and to connect them to other structures and to each other.

Various ZnO nanostructures, such as nanowires, nanobelts, nanobridges, nanonails, and hierarchical nanostructures, have been produced by various methods.<sup>3–7)</sup> In the vapor-based route, zinc species are in the vapor state and arise from the evaporation of pure zinc powder,<sup>8,9)</sup> zinc oxide powders,<sup>10)</sup> organic compounds, or mixtures of zinc oxide powder with powders of other materials.<sup>11)</sup> The composition of the source materials, the pressure of the vacuum and growth atmosphere, reaction temperature, substrate, and the type and amount of catalysts can all markedly change the morphology and nanostructure of the grown ZnO. In addition, studies focused on two-dimensional (2D) ZnO nanostructures, including nanowalls and nanosheets, are limited compared with those focused on one-dimensional ZnO nanostructures. It has been suggested that ZnO nanowalls can be used as energy-storage devices, chemical sensors, and solar cells owing to their large surface-to-volume ratio.<sup>12)</sup> In this regard, the assembly and synthesis of these nanostructures via a bottom-up method would be of strong potential importance.

In this work, we synthesized a ZnO nanowire/nanowall network on  $c\text{-Al}_2\text{O}_3$  at atmospheric pressure using a vapor phase epitaxy (VPE) method. We synthesized high-quality

ZnO nanowires on a ZnO nanowall with uniform sizes. We confirmed the structural properties of homojunctional ZnO nanowire/nanowall structures using X-ray diffraction (XRD) analysis and high-resolution transmission electron microscopy (HRTEM).

## 2. Experimental Procedure

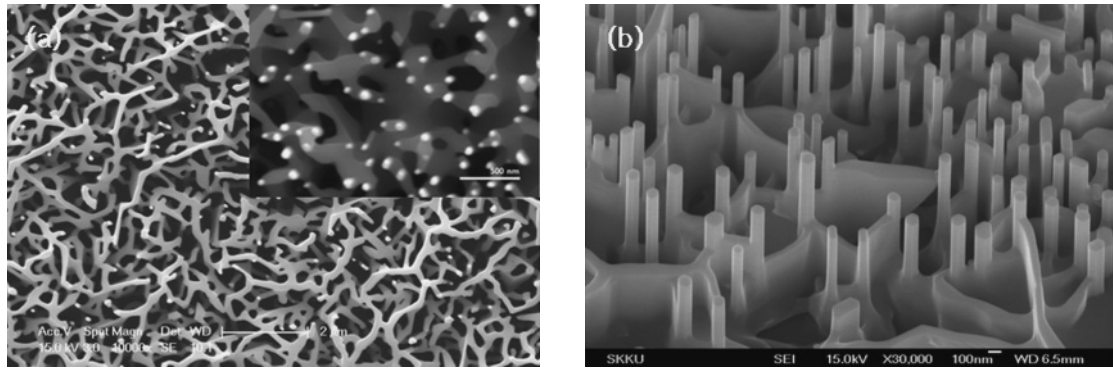
Homojunctional ZnO nanowire/nanowall structures were synthesized using a VPE method. The starting materials were ZnO and carbon powder with a 1 : 1 weight ratio. An Au thin film of 3 nm thickness was used as the catalyst for the growth of the ZnO nanostructures. High-purity Ar (99.999%) was used as the carrier gas. It was introduced at a flow rate of 1200 sccm into a quartz tube at atmospheric pressure (760 Torr). The main growth of the ZnO nanostructures was performed at 950–1050 °C. After the main growth, the ZnO nanostructures were cooled naturally to room temperature, and then analyzed by XRD analysis using a Bruker D8 Discover system with Cu K $\alpha$  radiation. The shapes and morphologies of the ZnO nanostructures were observed using field-emission scanning electron microscopy (FESEM) and HRTEM. The chemical composition of the ZnO nanostructures was analyzed using X-ray energy dispersion spectrometry (EDX). The structure of the homojunctional nanowire/nanowall structures was investigated using selected-area electron diffraction (SAED) analysis.

## 3. Results and Discussion

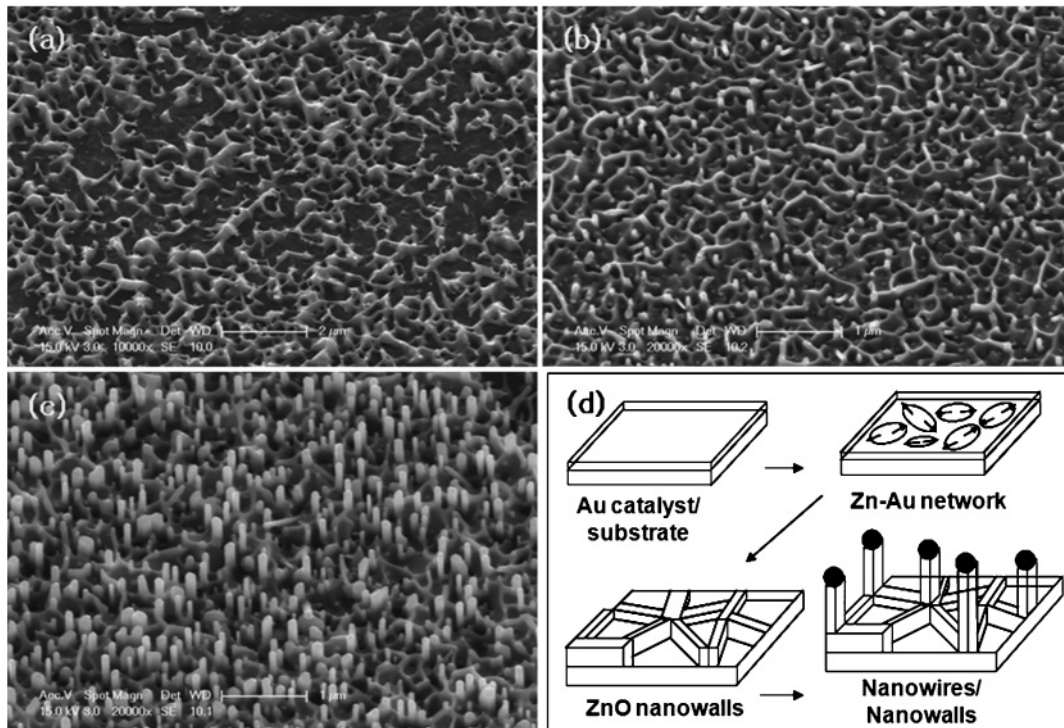
Figure 1(a) shows a top-view FESEM image of the homojunctional ZnO nanowire/nanowall structures and the inset shows a backscattered-electron (BSE)-mode FESEM image. Figure 1(b) shows an FESEM image of the homojunctional ZnO nanowire/nanowall structures grown by the help of the Au catalyst on the  $\text{Al}_2\text{O}_3$  surface. It can be seen that the homojunctional nanowire/nanowall structures are vertically well aligned having a random honeycomb-like pattern. As shown in Fig. 1(a), the metal catalyst only exists on the ends of the ZnO nanowires.

Figure 2 shows time-dependent FESEM images of the homojunctional nanowire/nanowall structures. Figures 2(a)–2(c) show the initial-, middle-, and end-stage images of the homojunctional ZnO nanowire/nanowall structures during their growth, respectively. As shown in Fig. 2, firstly, a Zn–Au solid solution network is formed on the  $c\text{-Al}_2\text{O}_3$

\*E-mail address: dhyoon@skku.edu



**Fig. 1.** FESEM images of homojunctional ZnO nanostructures synthesized by a VPE method. (a) Top-view image and the inset is a BSE-mode image. (b) Homojunctional ZnO nanostructures.



**Fig. 2.** Time-dependent FESEM images of homojunctional ZnO nanostructure. (a) Initial stage. (b) Middle stage. (c) End stage. (d) Schematic diagram of homojunctional ZnO nanostructure mechanism.

substrate. The ZnO nanowalls were directly grown on the Zn–Au alloy networks rather than the growth of ZnO nanowires via a vapor–liquid–solid (VLS) mechanism.<sup>13)</sup> We confirmed the chemical composition of ZnO nanostructures using EDX measurement, as shown in Fig. 3. The ZnO nanowalls consist of only the components of Zn and O without a Au catalyst. Secondly, the ZnO nanowalls then start to grow on the Zn–Au network surface [Figs. 2(a) and 2(b)]. Finally, the shapes of the ZnO nanowalls that are formed resemble those of the Zn–Au alloy networks. Then, the Au catalyst diffuses on the nanowall surfaces,<sup>14)</sup> aggregating at the nodes. Epitaxial ZnO growth is incited by the active sites of the ZnO network channels, such as the nodes regions. Due to the surface energy at the node increases with the resultant Au atoms diffusing and accumulating at the nodes for overall energy compensation.<sup>15,16)</sup> Therefore, ZnO nanowires begin to form from nodes via a VLS mechanism at the critical point [Fig. 2(c)].

Figure 2(d) shows a schematic diagram of the homojunctional ZnO nanowire/nanowall structures growth mechanism that is time-dependent.

Figure 4(a) shows a  $2\theta$  scan of the XRD pattern used for the structural characterization of the synthesized homojunctional ZnO nanowire/nanowall structures. All of the diffraction lines were indexed and identified by X-ray powder diffraction as the hexagonal wurtzite type, while no cubic phase was found. The peak of the synthesized homojunctional ZnO nanowire/nanowall structures was sharp and the full width at half-maximum has a narrow peak. Figure 4(b) shows a phi scan of the homojunctional ZnO nanostructures. The six fold rotational symmetry peak, with an equivalent distance of  $60^\circ$ , clearly indicates that the homojunctional ZnO nanowire/nanowall structures were epitaxially grown with homogeneous in-plane alignment  $c\text{-Al}_2\text{O}_3$  substrate. The XRD analysis shows that the homojunctional ZnO nanowire/nanowall structures are well crystallized.

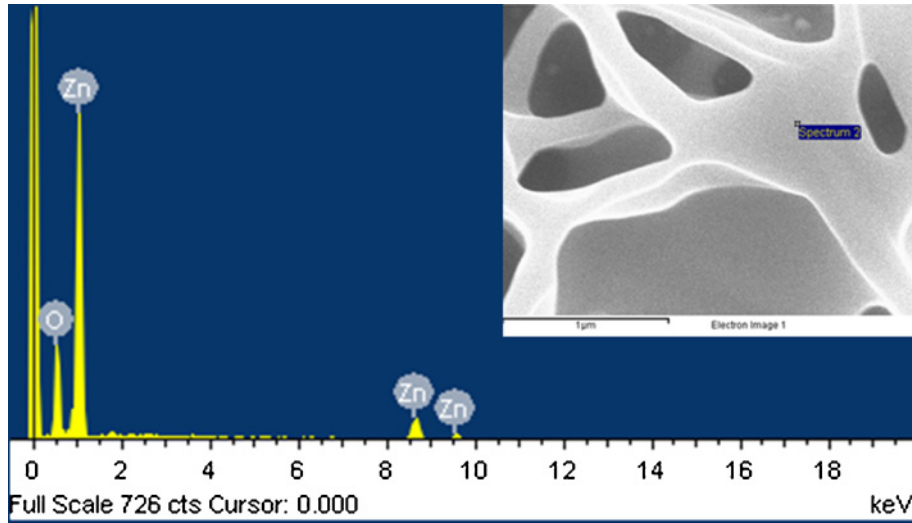


Fig. 3. (Color online) Chemical composition of ZnO nanowall obtained by EDX.

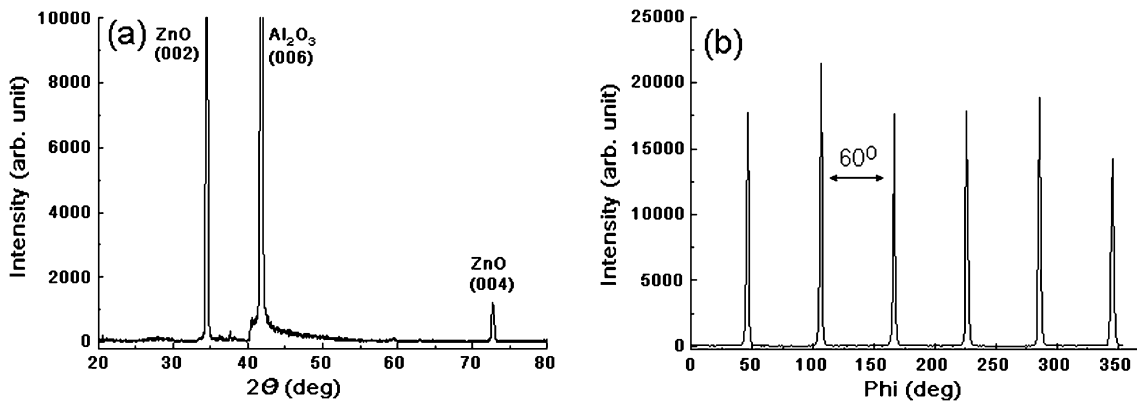


Fig. 4. XRD pattern of synthesized homojunctional ZnO nanostructures. (a) 2-Theta scan of homojunctional ZnO nanostructures. (b) Phi scan of homojunctional ZnO nanostructures.

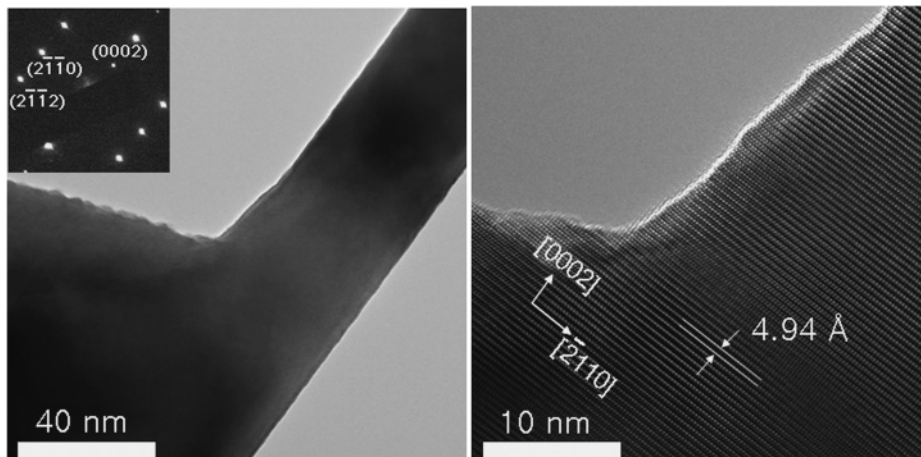


Fig. 5. TEM images of high-quality homojunctional ZnO nanostructures. (a) Low-magnification TEM image of homojunctional ZnO nanostructures. The inset is the SAED pattern of the TEM image. (b) High-magnification image of homojunctional ZnO nanostructures.

Figure 5(a) shows a low-magnification TEM image of the junctional area. The synthesized homojunctional ZnO nanowire/nanowall structures have a smooth morphology on the side edge and a clean surface without any loose particles. The inset in Fig. 5(a) shows the SAED pattern of

the homojunctional ZnO nanowire/nanowall structures. Figure 5(a) shows the homojunctional ZnO nanowire/nanowall structures to be single-crystalline, with good crystallinity, which was indexed to the diffraction pattern of hexagonal ZnO. The clear and regular spots reveal that the

synthesized homojunctional ZnO nanowire/nanowall structures possess high-quality single crystallinity, which indicates that the nanowires and nanowall have no orientation mismatch. Thus, we could conclude that the ZnO nanowires and nanowall form a single unit and are part of the same single crystal.

Figure 5(b) shows a high-magnification TEM image of the junctional area. The growth direction was [0002] in the hexagonal structure of the homojunctional ZnO nanowire/nanowall structures. The visible lattice is almost perfect and its crystallographic orientation is clear and uniform. While defects, such as dislocations, stacking faults or twins, are generally observed in junctional nanostructures,<sup>17)</sup> there were no observable defects in the junctional area of the ZnO nanowire/nanowall structures.

#### 4. Conclusions

We synthesized high-quality homojunctional nanowire/nanowall structures using a VPE method at atmospheric pressure. We could conclude that the ZnO nanowires and nanowall form a single unit and are part of the same single crystal. All of the experimental results confirm the good crystallinity of the synthesized homojunctional ZnO nanowire/nanowall structures. The formation of the homojunction structures is due to diffusion of the metal catalyst on the ZnO nanowall. The results obtained in this work can be applied to various device applications using self-assembled junction structures.

- 1) Y. Chen, D. M. Bagnall, H. Koh, K. Park, K. Hiraga, Z. Zhu, and T. Yao: *J. Appl. Phys.* **84** (1998) 3912.
- 2) D. J. Chen, X. W. Sun, and C. X. Xu: *Ceram. Int.* **30** (2004) 1725.
- 3) Y. W. Heo, V. Varadarajan, M. Kaufman, K. Kim, D. P. Norton, F. Ren, and P. H. Fleming: *Appl. Phys. Lett.* **81** (2002) 3046.
- 4) B. D. Yao, Y. F. Chan, and N. Wang: *Appl. Phys. Lett.* **81** (2002) 757.
- 5) Y. B. Li, Y. Bando, T. Sato, and K. Kurashima: *Appl. Phys. Lett.* **81** (2002) 144.
- 6) B. D. Yao, H. Z. Shi, H. J. Bi, and L. D. Zhang: *J. Phys.: Condens. Matter* **12** (2000) 6265.
- 7) K. K. Kim, J. H. Song, H. J. Jung, and S. J. Park: *J. Appl. Phys.* **87** (2000) 3573.
- 8) Y. W. Wang, L. D. Zhang, G. Z. Wang, X. S. Peng, Z. Q. Chu, and C. H. Liang: *J. Cryst. Growth* **234** (2002) 171.
- 9) S. C. Lyu, Y. Zhang, H. Ruh, H. J. Lee, H. W. Shim, E. K. Suh, and C. J. Lee: *Chem. Phys. Lett.* **363** (2002) 134.
- 10) K. Park, J.-S. Lee, M.-Y. Sung, and S. Kim: *Jpn. J. Appl. Phys.* **41** (2002) 7317.
- 11) M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. Yang: *Adv. Mater.* **13** (2001) 113.
- 12) S.-W. Kim, S. Fujita, M.-S. Yi, and D. H. Yoon: *Appl. Phys. Lett.* **88** (2006) 253114.
- 13) D. Zhao, C. Andreazza, P. Andreazza, J. Ma, Y. Liu, and D. Shen: *Chem. Phys. Lett.* **408** (2005) 335.
- 14) J. E. Allen, E. R. Hemesath, D. E. Perea, J. L. Lensch-Falk, Z. Y. Li, F. Yin, M. H. Gass, P. Wang, A. L. Bleloch, R. E. Palmer, and L. J. Lauhon: *Nat. Nanotechnol.* **3** (2008) 168.
- 15) S.-W. Kim, H. K. Park, M. S. Yi, N. M. Park, J. H. Park, S. H. Kim, S. L. Maeng, C. J. Choi, and S. E. Moon: *Appl. Phys. Lett.* **90** (2007) 033107.
- 16) H. T. Ng, J. Li, M. K. Smith, P. Nguyen, A. Cassell, J. Han, and M. Meyyappan: *Science* **300** (2003) 1249.
- 17) L. S. Karlsson, M. W. Larsson, J. Malm, L. R. Wallenberg, K. A. Dick, K. Deppert, W. Seifert, and L. Samuelson: *NANO* **2** (2006) 139.