Synthesis of Functional ZnO Nanowall Networks Using Simple Solution Etching

Brijesh Kumar¹, Kyung-Sik Shin¹, Min-Su Yi², Sang Yeol Lee³, and Sang-Woo Kim¹, 4

¹School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, China
²Center for Energy Materials Research, Department of Materials Science and Engineering, Kyungpook National University, Sangju 742-711, Republic of Korea
³Department of Semiconductor Engineering, Cheongju University, Cheongju, 360-764 Chungbuk, Republic of Korea
⁴Center for Human Interface Nanotechnology (HINT), SKKU-Samsung Graphene Center, Center for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), Sungkyunkwan University (SKKU), Suwon 440-746, Republic of Korea

We report the synthesis of high quality single crystalline ZnO nanowall networks (NNs) using ammonia solution etching of a ZnO nanowire-nanowall heterojunction (NNH) structure. Synchrotron X-ray diffraction revealed that the full-width-at-half-maximum of the ZnO (0002) peak in the ZnO NN sample was much narrower than that of the ZnO NNH sample. Temperature-dependent photoluminescence (PL) measurements revealed more intense and narrower bound exciton peak emission in the NN sample compared to that in the NNH sample. Moreover, the clear observation of free exciton emission in the PL spectrum of the NN sample, even at temperatures as low as 30 K, suggested incorporation of a small number of impurities into the NN sample. In addition, I–V characteristics confirm the higher conductivity of the ZnO NNs as compared to those of the NNH structures, indicating that the NN sample had a superior crystalline property than NNH sample.

Keywords: ZnO, Nanowall Network, Nanowire, Heterojunction, Chemical Vapor Deposition, Solution Etching.

1. INTRODUCTION

Two-dimensional (2D) layered nanostructures, such as graphene, nanosheets, nanodiskettes, and nanowalls,¹–⁴ have attracted considerable interest in the nano-material research because of their possible applications as chemical and biological sensors, energy storage devices, and energy harvesting devices due to their high surface areas and ease of manipulation. However, 2D layered nanostructures have attracted less attention because of difficulty in controlling their morphologies and dimensions compared to those of 0D and 1D nanostructures, such as nanoparticles, nanowires, nanorods, and nanotubes.

Much effort to synthesize 2D layered nanostructures has been made.¹–⁴ Semiconducting ZnO nanowall structures with a uniform thickness and width have been produced using a range of techniques including dry processes⁵–⁶ such as thermal chemical vapor deposition (CVD) and metal organic chemical vapor deposition (MOCVD) as well as solution-based chemistry techniques⁷–⁹ such as hydrothermal, sol–gel, and electrochemical deposition. These semiconducting ZnO nanowall structures have been reported to exhibit a crystalline nature and to have effective gas sensing properties.¹⁰ However, nanostructures synthesized using solution methods are not considered to be the best option for highly efficient device applications because they contain a large number of point defects and unwanted surface states.¹¹ In addition, despite the many reports of ZnO nanowalls grown via dry processes, the growth of ZnO nanowall structures is quite sensitive to the growth conditions, resulting in the lack of reproducibility and controllability.¹¹

Although putative mechanisms for ZnO nanowall formation on Al₂O₃ or Si substrates with GaN or ZnO buffer layers have been proposed, the lack of rational control often results in nanowalls with aligned ZnO nanowires that are positioned directly above a single-phased nanowall structure.¹⁰ The frequent formation of nanowire-nanowall heterojunction (NNH) structures in the dry process is undesirable for 2D nanostructure-based device applications. Here, we report a general method for synthesizing...
ZnO nanowall networks (NNs) through simple solution etching of a ZnO NNH structure. Synchrotron X-ray scattering experiments and the temperature-dependent photoluminescence (PL) spectra of the NN sample prepared through the selective etching of nanorods onto nanowalls revealed dramatic improvements in the crystalline and optical properties of the NN sample compared to those of the NNH sample.

2. EXPERIMENTAL DETAILS
ZnO NNH structures were synthesized in a horizontal tube furnace using thermal CVD. A gold (Au) layer (4 nm) was coated onto c-plane Al₂O₃ substrates as a catalyst for the growth of highly aligned ZnO NNH arrays via thermal evaporation. ZnO NNH arrays were obtained through a carbothermal reaction by evaporating a mixture of ZnO (99.999% purity) and graphite (99.999% purity) powder (1:1) in an Ar atmosphere. A quartz boat containing both the substrate and powder mixture was placed in the central hot zone inside the tube furnace. Once the Ar gas flow had stabilized at 1000 standard cubic centimeters per minute (sccm), the tube was heated to 1030 °C for 60 min. Solution etching of ZnO NNH arrays to produce ZnO NNs was performed using an ammonia solution in deionized water (50 ml and 50 ml, respectively) for 15 min. Pure single crystalline NN structures were reproduced using the same etching conditions as those used for the other NNH samples.

The morphologies of the as-grown and etched samples were examined using field-emission scanning electron microscopy (FE-SEM). The structural properties of the samples were investigated using synchrotron X-ray scattering measurements that were carried out at the 5C2 beamline at the Pohang Light Source. The synchrotron X-rays were focused vertically using a mirror and a double bounce Si (111) monochromator. Temperature-dependent PL measurements using the 325-nm line of a continuous wave He–Cd laser were carried out to investigate the optical properties of the samples. Further, to confirm the higher conductivity and functionality of the ZnO NNs as compared to those of the NNH structures, the current–voltage (I–V) characteristics of the samples were measured using CompactStat Instrument of IVIUM Technology in the dark. Gold and silver electrodes with a separation of 7 mm were patterned with a shadow mask on top of the NNs and NNH structures using thermal evaporation.

3. RESULTS AND DISCUSSION
FE-SEM images of the ZnO NNH and ZnO NN samples are shown in Figure 1. The NNH structures were vertically aligned with a honeycomb-like pattern, consistent with the results of a previous report. The height and diameter of the nanorods were approximately 300~600 nm and 40~80 nm, respectively, and the nanowall thickness and height were approximately 80~100 nm and ~150 nm, respectively. There were small variations due to the non-flat top surfaces of the ZnO nanowalls, and ZnO NNH structures grew only in the Au catalyst-coated area. This suggests that Au plays an important role in the formation of ZnO NNH structures. In the ZnO NNH structure, the nanorods grew rapidly under the Au catalysts through a vapor–liquid–solid (VLS) process, and nanowall networks in between the nanorods (catalyst-free region) grew at a much slower rate through a vapor–solid (VS) process. The formation of nanorods can prevent the ZnO vapor from reaching the bottom of the network, further limiting nanowall network growth.

ZnO NNs prepared through the selective etching of nanorods in the ZnO NNH structure had relatively flatter top surfaces than the ZnO NNH structures, as shown in Figure 1(b). In addition, the thickness and height of the nanowalls were almost uniform, which suggests that etching produced an undercut of the nanorods on the NNs. In the etching step, the dissolution of ZnO proceeds at room temperature according to Eq. (1):

\[ \text{ZnO} + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{Zn(NH}_3)_2^2\text{+ (aq)} + \text{OH}^- \]  

We attributed the fast etching (40 nm/min) of nanorods in the NNH structure to preferential etching along the polar axis, the curvature dependence of NH₃ molecule absorption on the nanorod tips, and the defect-enriched nature of the nanorods.
of the samples caused by the rapid growth of nanorods through the VLS process. The ZnO NNs were barely etched during the etching process, possibly because only a few structural imperfections were present in the NNs grown through the VS process. These results indicate that the etch rate of ZnO nanorods is much higher than that of ZnO NNs in the ZnO NNH structure.

Powder diffraction profiles of the ZnO NNH and NN structures on c-plane Al$_2$O$_3$ substrates are shown in Figure 2. The scans were taken along the surface normal direction, $Q_z = 4\pi \sin(\theta/2)/\lambda$, in reciprocal space. The diffraction peaks at $Q_z = 2.412$ Å$^{-1}$ in both samples are related to ZnO (0002) Bragg reflection, suggesting that ZnO NNHs and NNs have a c-axis orientation in the surface normal direction. The peak at $Q_z = 2.662$ Å$^{-1}$ from the ZnO NNH sample was shifted slightly from the position of pure Au (111) due to the incorporation of Zn into Au (111), as expected for high temperature CVD growth. In contrast, $Q_z = 2.669$ Å$^{-1}$ for the ZnO NN sample was assigned to an almost pure Au (111) phase (Joint Committee on Powder Diffraction Standards $Q_z = 2.668$ Å$^{-1}$). The full widths at half maximum (FWHM) of the ZnO (0002) peaks from the ZnO NNH and NN samples were 0.026 Å$^{-1}$ and 0.023 Å$^{-1}$, respectively. This suggests that the crystallinity of the NN sample was not adversely affected by the solution etching process; in fact, it improved significantly. The improvement in the crystalline quality of the NN sample is due to the removal of defect-rich nanorods that were grown through the VLS process.

Figure 3 shows the scattering profiles along the azimuth circle of the nonspecular ZnO (1012) and Au (111) for both ZnO NNH and NN samples. ZnO had an epitaxial relationship with Au, and the phi scan of the nonspecular ZnO (1012) and Au (111) reflections showed six-fold symmetry due to the formation of anti-domains in Au. As shown in Figure 3(a), a broad Au (111) peak was observed in the ZnO NNH sample, which originated from Au–Zn alloys on the top of the ZnO nanorods, as expected in the VLS process. In contrast, in the ZnO NN sample, a very sharp Au (111) peak was obtained due to clear selective etching of the nanorods with Au–Zn tips, as shown in Figure 3(b). Therefore, only pure Au exists in the NNs, resulting in a sharp Au (111) reflection.

Figure 4 shows the temperature-dependent PL spectra of the NNH and NN samples as a function of temperature.
from 30 K to 100 K. A broad peak at 3.357 eV with a FWHM of approximately 35 meV at 30 K was observed for the NNH structure (Fig. 4(a)); this broad peak is related to the neutral donor bound exciton ($D^{+}X$). In contrast, the intense and narrow emission peak of the NN sample at 3.355 eV with a FWHM of 8 meV at 30 K was assigned to the characteristic $D^{+}X$ peak (Fig. 4(b)). A peak at 3.375 eV was also observed in the PL spectrum of the NN sample at 30 K, related to free-exciton (FX) recombination. In addition, the size of the FX peak increased and was red-shifted because of the decrease in band-gap with increasing temperature and broadening of the PL peaks due to the phonon effect.

The narrow and intense peak as well as the observation of a FX emission peak as a shoulder of the $D^{+}X$ peak in the temperature-dependent PL spectra of the NN sample indicate the increased crystallinity compared to that of the NNH sample, whose PL spectrum was characterized by the absence of FX emission and broadening of the $D^{+}X$ peak due to the presence of impurities. The well-resolved excitonic emission of the NN sample indicates high crystal quality, consistent with the XRD results. A very small peak shift in the $D^{+}X$ peak of 2 meV from 3.357 eV to 3.355 eV was attributed to the presence of a small amount of stress in the surface atoms of the NN sample prepared through etching. The peaks at approximately 3.315 eV and 3.289 eV, which were assigned to the FX-first phonon replica (1LO) and $D^{+}X$-1LO, respectively, were well resolved in the NN sample because of the enhanced crystalline quality as well as the small number of impurities.

The enhancement in the crystalline qualities of the NNs compared to that of the NNH structure was confirmed by $I$–$V$ measurements in the dark. The linear $I$–$V$ relations under both forward and reverse biases exhibited metal-semiconductor ohmic contact. The calculated resistances of the ZnO NN and NNH samples from the $I$–$V$ curve measurements in the dark were 400 $\Omega$ and 900 $\Omega$, respectively, which confirm that the NN sample was more conductive than was the NNH structure as illustrated in Figure 5. We hypothesize that the superior conductivity performance of the NN sample is due to the better metal-semiconductor ohmic contacts of the electrodes at the top surface, and its higher crystallinity compared to those of the NNH sample.

4. CONCLUSION

High quality single crystalline ZnO NNs were produced through solution etching of ZnO NNH structures. Synchrotron X-ray diffraction showed that the crystallinities of the NN samples were not deteriorate during the solution etching process and in fact were improved significantly because of the removal of defect-rich nanorods.
during etching. The narrow, intense FX emission peak was observed as a shoulder of the D\textsuperscript{4}X peak in the temperature-dependent PL spectrum of the NN sample and indicated that the NN sample was more crystalline and had fewer impurities than did the NNH sample. The NN sample shows higher conductivity compared to that of the NNH sample, indicating that the NN sample possessed a superior crystalline property compared to that of the NNH sample.

Acknowledgment: This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (MEST) (2012R1A2A1A01002787) and the Energy International Collaboration Research and Development Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) funded by the Ministry of Knowledge Economy (MKE) (2011-8520010050).

References and Notes


Received: 19 March 2011. Accepted: 29 August 2012.