640 *Journal of Electrical Engineering & Technology Vol. 5, No. 4, pp. 640~645, 2010*
DOI: 10.5370/JEET.2010.5.4.640

Power Generating Characteristics of Zinc Oxide Nanorods Grown on a Flexible Substrate by a Hydrothermal Method

Jae-hoon Choi†, Xueqiu You*, Chul Kim, Jungil Park* and James Jungho Pak*,****

Abstract – This paper describes the power generating property of hydrothermally grown ZnO nanorods on a flexible polyethersulfone (PES) substrate. The piezoelectric currents generated by the ZnO nanorods were measured when bending the ZnO nanorod by using I-AFM, and the measured piezoelectric currents ranged from 60 to 100 pA. When the PtIr coated tip bends a ZnO nanorod, piezoelectrical asymmetric potential is created on the nanorod surface. The Schottky barrier at the ZnO-metal interface accumulates elecntrons and then release very quickly generating the currents when the tip moves from tensile to compressed part of ZnO nanorod. These ZnO nanorods were grown almost vertically with the length of 300-500 nm and the diameter of 30-60 nm on the Ag/Ti/PES substrate at 90°C for 6 hours by hydrothermal method. The metal-semiconductor interface property was evaluated by using a HP 4145B Semiconductor Parameter Analyzer and the piezoelectric effect of the ZnO nanorods were evaluated by using an I-AFM. From the measured *I-V* characteristics, it was observed that ZnO-Ag and ZnO-Au metal-semiconductor interfaces showed an ohmic and a Schottky contact characteristics, respectively. ANSYS finite element simulation was performed in order to understand the power generation mechanism of the ZnO nanorods under applied external stress theoretically.

Keywords: Hydrothermal method, I-AFM, Piezoelectric effect, Schottky contact, Zinc oxide

1. Introduction

Nanoscale semiconductor materials have attracted great interests of researchers because of their importance not only in fundamental research areas but also in practical applications. Among many nanoscale semiconductor materials, ZnO is a typical piezoelectric inorganic semiconducting material, which has a wide direct band gap of 3.37 eV, a large excitation binding energy of 60 meV, piezoelectricity, excellent chemical and thermal stability, and biocompatibility [1], [2]. In order to grow ZnO nanostructures, various techniques have been developed for the synthesis of the ZnO nanostructures including vapor–liquid–solid (VLS) method, chemical vapor deposition (CVD), and hydrothermal method [3]-[6]. VLS and CVD methods require sophisticated equipments and strict conditions such as single-crystalline substrates, relatively high process temperature (>500 °C), and vacuum conditions (~10^{-2} Torr) [7]. The hydrothermal method is substrate independent, convenient, and low cost for large-scale preparation of well-ordered ZnO nanorod arrays.

Recently, ZnO nanostructures have been studied for power generating devices due to piezoelectric and semiconducting properties of ZnO [8]. The ZnO nanorods can be used in systems such as foldable or reformable power source, artificial skins, touch sensors and flexible displays because it is possible for ZnO nanostructures to generate the current and potential under an external mechanical strain [9].

This paper describes the power generating properties of hydrothermally grown ZnO nanorods on a flexible polyethersulfone (PES) substrate. The ZnO nanorods were grown successfully on the flexible substrate by a hydrothermal method, and then they were evaluated by using a scanning electron microscopy (SEM) and an energy dispersive X-ray analysis (EDX). The power generating properties of the ZnO nanorods were examined by using a conductive atomic force microscopy (I-AFM) and the HP 4145B Semiconductor Parameter Analyzer. Also, the stress-strain distributions for the ZnO nanorods were analyzed by using ANSYS finite element analysis software.

2. Experiments

2.1 Materials and Chemicals

All the chemicals used in the fabrication process are commercially available and they were used without further purification since they are of electronic grade. Sodium hydroxide (NaOH), zinc nitrate hexahydrate, zinc acetate dehydrate, and hexamethylenetriamine (HMTA) were purchased from Sigma-Aldrich.

† Corresponding Author: School of Electrical Engineering, Korea University, Korea.
* School of Electrical Engineering, Korea University, Korea. (pak@korea.ac.kr)
** Department of Micro/Nano Systems, Korea University, Korea. (pak@korea.ac.kr)
Received: March 23, 2010; Accepted: July 21, 2010

2.2 Growth of ZnO Nanorods on Flexible PES Substrate

Fig. 1 shows the fabrication procedure of growing ZnO nanorods on a flexible PES substrate. PES film (4 cm × 4 cm and 500 μm thick) was used as a starting flexible substrate and a thin Ti layer was deposited on the PES film by e-beam evaporation as an adhesion layer. Ag was subsequently deposited on the Ti/PES substrate by thermal evaporation. ZnO nanorods on the PES were prepared by a hydrothermal method. A mixture of 30 mM NaOH solution in methanol and 10 mM zinc acetate dehydrate in methanol was used as a seed solution for the ZnO nanorods under stirring at 60°C for 2 hours. This seed solution was spin-coated onto a Ag/Ti/PES substrate at 1000 rpm for 30 s. The uniformity and density of the ZnO seed layer on the substrate depend on the spin-coating speed and time [10], [11]. Also, the density of ZnO nanorods depends on the density of ZnO seed layer [11]. After coating the ZnO seed layer, the substrate was dried and annealed at 150 °C for 10 min to enhance the seed layer adhesion to the substrate. ZnO nanorods were then formed in a growth solution, which was a mixture of 25 mM HMTA and 25 mM zinc nitrate hexahydrate in this experiment at 90°C for 6 hours [12]. The substrate was then rinsed with deionized water and dried with N_2 gas.

2.3 Characteristics Evaluation of ZnO Nanorods

The geometry of the grown ZnO nanorods was observed by using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4300). The element composition of the ZnO nanorods was examined by using an energy dispersive X-ray spectroscope (EDX, Horiba EX-200). The contacts between ZnO nanorods and metal electrodes (Ag or Au) were evaluated by using HP 4145B semiconductor parameter analyzer.

Both *I-V* characteristic curves of a ZnO nanorod and the generating currents from the bending ZnO nanorods were measured by using the I-AFM (XE-100, PSIA) in contact mode. Fig. 2 shows the schematic illustration of an I-AFM based measurement setup for measuring *I-V* characteristics and piezoelectric effect of the grown ZnO nanorods. The bottom of ZnO nanorods was electrically connected to a metal holder through conductive silver paste. The free ends of the ZnO nanorods were bent by using a 30 nm radius I-AFM Si tip which is coated with alloyed PtIr. In order to measure the *I-V* characteristic curves of a single ZnO nanorod, a PtIr coated Si tip was used in static contact with the top of a single ZnO nanorod. A voltage was swept from -2.7 to 2.7 V between the ZnO nanorod and the I-AFM tip, and then the current was measured by I-AFM. For measuring the current generated by bending ZnO nanorods, ZnO nanorods were bent by scanning the I-AFM tip over the ZnO nanorods. This current was measured between the I-AFM tip and the metal holder at zero applied voltage.

In order to understand the piezoelectric characteristic of each ZnO nanorod theoretically, a three-dimensional (3-D) stress-strain simulation was performed when a ZnO nanorod was bent by using ANSYS (ANSYS. Inc.), a finite element simulation tool.

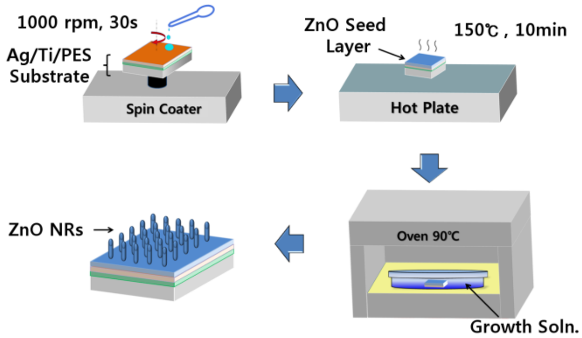


Fig. 1. Schematic illustration: fabrication of ZnO nanorods on the Ag/Ti/PES substrate by a hydrothermal method.

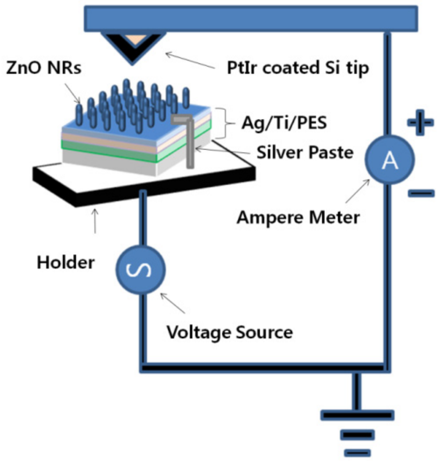
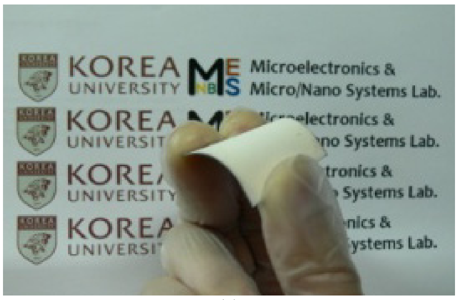


Fig. 2. Schematic of I-AFM based measurement setup for the *I-V* characteristics and piezoelectric effect of ZnO nanorods.

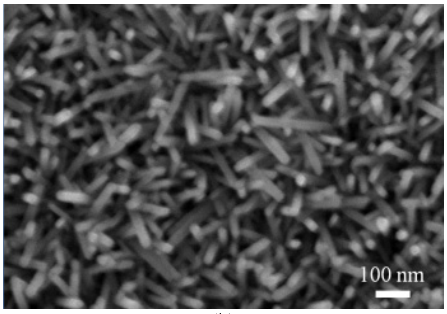
3. Results and Discussion

Fig. 3 shows the SEM images of the grown ZnO nanorods on the Ag/Ti/PES substrate. ZnO nanorods were quite uniformly grown with the length of 300-500 nm and the diameter 30-50 nm as shown in Fig. 3(b). The nanorod number density can be as high as five billion rods per cm^2. The cross-section SEM image (Fig. 3c) shows that the ZnO nanorods were grown almost vertically. From the EDX spectrum result in Fig. 4, the atomic ratio of Zn to O is calculated to be 1:1.01, confirming the purity of ZnO nanorods.

The linear *I-V* curve in Fig. 5(a) clearly indicates that ZnO-Ag interface formed an ohmic contact. It has been reported that there is no electron energy barrier at the interface because the electron affinity of ZnO is 4.5 eV and the work function of Ag is 4.26 eV [9]. While Fig. 5(b) shows a Schottky contact characteristic between the Au electrode and the grown ZnO nanorods. Because the work function of Au is 5.10 eV [13], which is substantially greater than the electron affinity of ZnO, there is an electron energy barrier at the interface.



(a)



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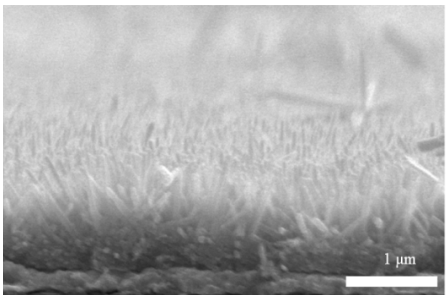


(c)

Fig. 3. ZnO nanorods on a Ag/Ti coated PES substrate. (a) Photographic image of the flexible ZnO nanorods. SEM images of the ZnO nanorods uniformly grown on a flexible substrate (b) top view and (c) cross-section view.

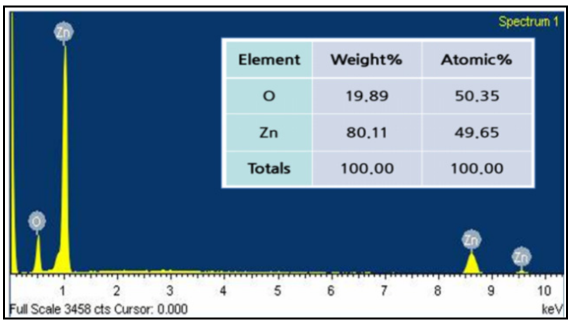
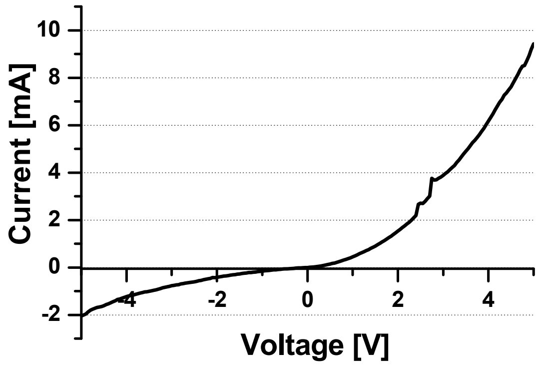
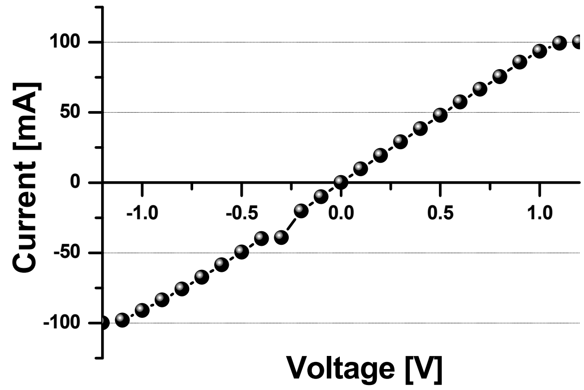


Fig. 4. The EDX spectrum of the grown ZnO nanorods on a flexible PES substrate. The inserted table shows the weight percentage and atomic percentage of the ZnO nanorods element composition.



(a)



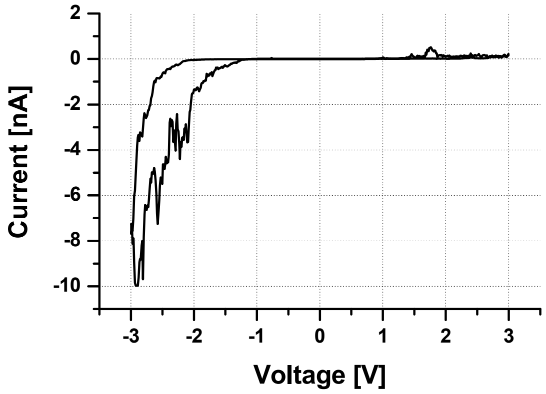
(b)

Fig. 5. *I-V* curves of (a) ZnO nanorods-Ag contact and (b) ZnO nanorods-Au contact.

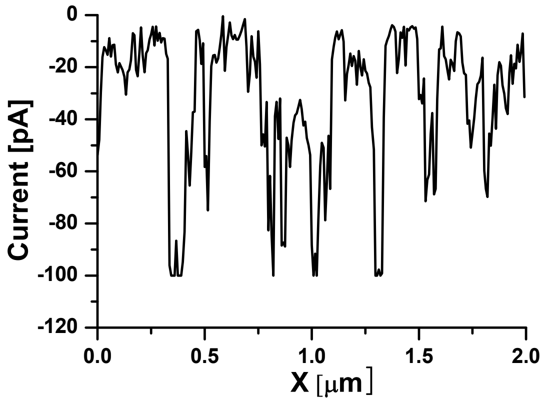
As shown in Fig. 6(a), the measured *I-V* curves between the alloyed PtIr coated I-AFM tip and the grown ZnO nanorod showed a Schottky contact curve. The negative current means that the currents flow from the grounded end to the tip. When a force of 200 nN was applied by scanning the I-AFM tip (spring constant of 0.2 N/m), 60-100 pA negative currents were measured by using the I-AFM as shown in Fig. 6(b).

The ANSYS simulation results showed the stress-strain distributions when the ZnO nanorods were bent by using the AFM tip in Fig. 7. The 3-D stress-strain simulation was performed with a ZnO nanorod of diameter 40 nm and length 400 nm which has the elastic modulus (Young's modulus) of about 170 GPa [14], the Poisson's ratio of 0.303 [15]. The ZnO nanorod was modeled as a solid cylinder shape as shown in Fig. 7(a). The bottom of the ZnO nanorod was fixed on the surface of substrate. For bending the nanorod, 200 nN force at the top of ZnO nanorod was applied. Fig. 7(b) shows the negative strain caused by compression and the positive strain caused by expansion. From the piezoelectric effect, the compressed surface has relatively negative potential compared to the tensile surface [16]. The principle of current-output process is accumulating/releasing electrons at/from the interface between the I-AFM tip and ZnO nanorod. When the I-AFM tip bends the ZnO nanorod, a positive potential is induced on the tensile surface. The electrons from the grounded I-AFM tip move to the PtIr coated tip. Reverse biased Schottky barrier with

ZnO nanorods block the electron's moving from the tip to the ZnO nanorod. As the tip moves to the compressed surface with negative potential, the tip has a forward biased Schottky barrier with the ZnO nanorod. Because the potential of the I-AFM tip is higher than the potential of compressed ZnO nanorod, the accumulated electrons on the tip release very quickly and generate the current signals. Therefore 60-100 pA negative currents were measured.

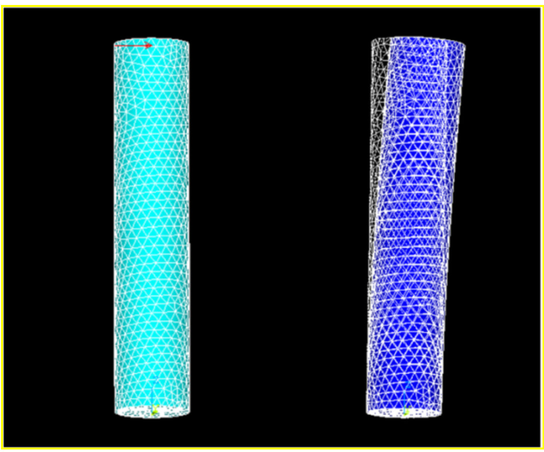


(a)

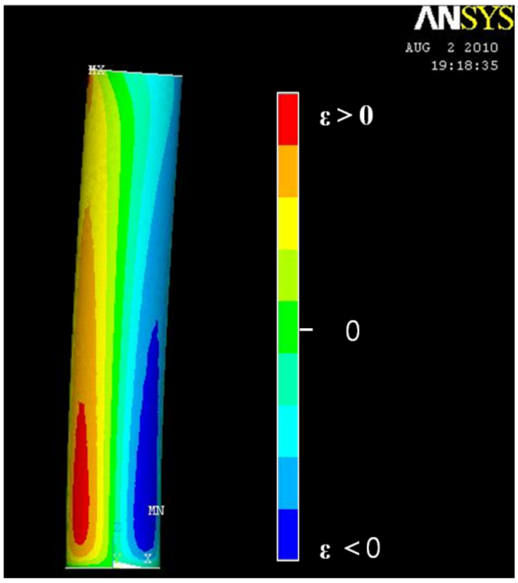


(b)

Fig. 6. (a) *I-V* curves of ZnO/PtIr coated Si tip, showing a Schottky contact curve. (b) The output current signals generated by ZnO nanorods when scanned by I-AFM tip.



(a)



(b)

Fig. 7. The stress-strain distributions of ANSYS simulation. (a) Schematic of ZnO nanorod bent by 200 nN on top of the nanorod. (b) The calculated strain ε distribution of deformed ZnO nanorod.

4. Conclusion

ZnO nanorods were uniformly synthesized on a Ag/Ti/PES flexible substrate by using a simple hydrothermal method. ZnO nanorods were almost vertically grown with 300-500 nm lengths and 30-50 nm diameters. The ohmic contact formation of ZnO-Ag and Schottky contact formation of ZnO-Au have been demonstrated by *I-V* characteristic curves from semiconductor parameter analyzer. 60-100 pA negative currents were obtained from the I-AFM tip in contact mode AFM measurements. The power generation based on piezoelectric property of ZnO nanorods can be explained by stress-strain distribution analysis by finite element method simulation and I-AFM results. The combination of metal-semiconductor interface property and piezoelectric property of ZnO nanorods realize the power generation

Acknowledgements

This research was supported by Seoul R&BD Program (No. 10920) and the National Research Foundation of Korea through a grant provided by Ministry of Education, Science and Technology in 2009(No. K20601000002-09E0100-00200). The authors are grateful to Park Systems Corp. for their help in measuring the piezoelectric current from the hydrothermally grown ZnO nanorods with their I-AFM.

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Jae-hoon Choi received BS degree in electrical engineering from Konkuk University. From 2009 he has studied for his MS degree at the School of Electrical Engineering at Korea University. His research interests are ZnO nano materials, superhydrophobic surface technology and ZnO based light emitting diode.

Xueqiu You received BS degree in electrical engineering in 2008 at Harbin institute of technology. He is currently an integrated MS and PhD student in the School of Electrical Engineering at Korea University. His research interests are ZnO and graphene nanostructures synthesis and applications.

Chul Kim received BS degree in control and instrument engineering from Korea University. From 2010 he has studied for his MS degree at the Department of Micro/Nano systems at Korea University. His research interests are blood flow rate sensor and ANSYS simulation in MEMS and microfluidics.

Jungil Park He received his BS degree in Division of Electronics and Information Engineering in 2004 at Korea University. He is currently an integrated MS and PhD student in the School of Electrical Engineering at Korea University. His research interests are microfabricated oxygen sensor and ZnO-based biosensor.

James Jungho Pak James Jungho Pak received his BS, MS and PhD degrees in Electrical Engineering respectively in 1985, 1988 and 1992 at Purdue University. He had worked in Intel Corporation in Santa Clara, CA, USA from 1992 to 1995 as a senior device physicist. Since 1995, he has been a professor in the School of Electrical Engineering at Korea University. His research interests include the Microsystems including bio-MEMS, biosensor, applications of polymer in microsensors and microactuators, flexible electronics and novel semiconductor devices and processing.