CONTROL OF OUTPUT MODE IN TRANSPARENT FLEXIBLE PIEZOELECTRIC NANOGENERATORS

D. Choi*
Department of Mechanical Engineering, Kyung Hee University, Yongin, Republic of Korea
*Corresponding author (dchoi@khu.ac.kr)

Keywords: *Piezoelectricity; Nanogenerator; Mode Control; Schottky contact; Morphology*

1. Introduction

Nanogenerators (NGs) that are driven by lateral bending of zinc oxide (ZnO) nanowires using atomic force microscope tip scanning[1] and ultrasonic vibration[2] have shown direct-current (DC)-type charge generation due to the coupled semiconducting and piezoelectric properties of ZnO.[1-3] The key element in such NGs is the placement of a Schottky barrier between the ZnO nanowire and an electrode, by which carriers are accumulated and released. Alternating-current (AC)-type power generation have also been investigated from stretching or bending of laterally packaged ZnO fine microscale wires and from direct compression of vertically-aligned ZnO nanowires.[4-7] In these cases, the Schottky barrier formed between the ZnO wires and the electrode acts as a gate that prevents the carriers from being transported through the interface between the wire and the electrode, and also leads to the accumulation of charges, thus providing a higher discharge rate. Thus, from previous charge generation behaviors of AC and DC modes, it can be seen that the charge generation behaviors were mainly dependent to the external operating loads such as ultrasonic vibration for lateral deformation of ZnO nanowires or compressive pressure for vertical deformation of nanowires. Furthermore, it is clear that the Schottky barrier between ZnO and electrodes is critical to enhance the output performance of charge generation from NGs.

Recently, our group has presented the first demonstration of large-scale transparent flexible (TF) NGs that are operated by flexing the device itself, showing DC-type charge generation.[8-10] Such TF-NGs lead to new types of embeddable energy harvesting technologies and new implications such as deformable mobile electronics or tactile skin sensors. For TF-NGs, ZnO nanorods are grown on a flexible polymer substrate by an aqueous solution method, where the transparency can be controlled by the density of the seed layer provided for ZnO growth. Interestingly, it was found that controlling seed density can lead to different ZnO nanorod morphologies during solution-based growth of ZnO.

In this work, we first report the charge-generating mode control in TF-NGs with a same device structure only according to the morphology of the ZnO nanorods without any use of an AC/DC converter. It is demonstrated that when the density of the seed layer for ZnO growth is higher it yields mostly vertically-aligned ZnO nanorods, on which AC-type charges are generated under a pushing load, while tilted ZnO nanorods grown on seed layers with low density generate DC-type charges under the same external load. We analyze and discuss the mode transition mechanism for the geometry-induced charge generation from TF-NGs under a pushing load.

2. Results and Discussion

Figure 1 illustrates the growth of ZnO nanorods using the aqueous solution method on a flexible plastic substrate.[8-10] ZnO nanorods grew with different morphologies depending on the density of the zinc acetate ($Zn(CH_3COO)_2$) seed layer. Specifically, when a seed solution of

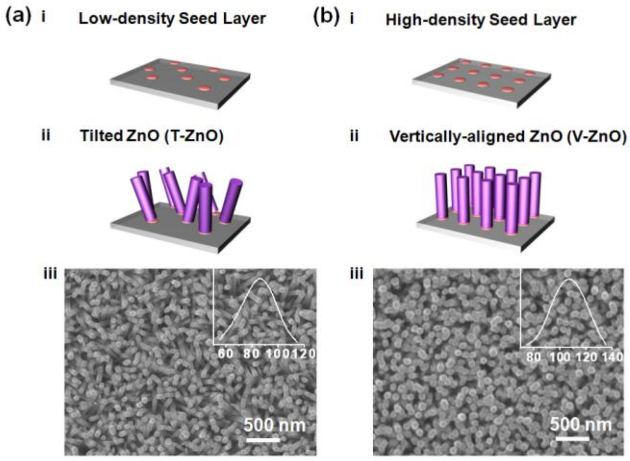

Fig.1. ZnO nanorods morphologies according to the seed density.

0.01 M concentration was spin-coated on a flexible ITO-coated plastic substrate, a seed layer with a low-density (Fig. 1a (i)) was formed, whereas a high-density seed layer (Fig. 1b (i)) was formed from a seed solution of 0.03 M. After growth, we observed the differing morphologies of the ZnO nanorods. As shown in Figures 1a (ii) and 1a (iii), primarily tilted ZnO nanorods (T-ZnO) were obtained on the low-density seed layer. However, vertically-aligned ZnO nanorods (V-ZnO) were obtained on the high-density seed layer (see Figs. 1b (ii) and 1b (iii)). Furthermore, we observed dimensional differences in ZnO nanorods according to the density of the seed layer. T-ZnO nanorods on a low-density seed exhibited diameters of 80-90 nm and a density of 45 rods/mm^2, as shown in Figure 1a (iii). ZnO nanorods with a larger diameters of 100-110 nm and higher densities of 53 rods/mm^2 were observed on high-density seed layers, as shown in Figure 1b (iii). We attribute the morphological change of ZnO nanorods to interfacial tension, which is strongly dominated by various factors such as the crystal orientation of the seed surface and seed density. The high-density seed layer (Fig. 1b (i)) is of the more preferred [001] orientation and has more crystallites than the low-density seed layer (Fig. 1a (i)), which results in the formation of vertically well-aligned ZnO nanorods with a high density in accordance with the previous work.[11-14]

In order to examine the orientation of as-grown ZnO nanorods with different morphologies, we measured X-ray diffraction (XRD) for V-ZnO nanorods and T-ZnO nanorods (see Supporting Information, Fig. S1). In general, ZnO shows a preferred orientation in the [001] direction due to the main polarity. Thus, as expected, XRD spectra show that both types of ZnO nanorods are mainly grown in the direction of the (002) plane. However, diffraction peaks of (101) and (102) planes are observed only from T-ZnO nanorods due to the scattering from tilted sides of the ZnO nanorods. Thus, we could confirm that the V-ZnO nanorods produced on high-density seeds are mostly well aligned, but that the T-ZnO nanorods grown on low-density seeds are mostly tilted.

It was found that DC-type chage output is generated from ZnO nanorods (i.e., T-ZnO)

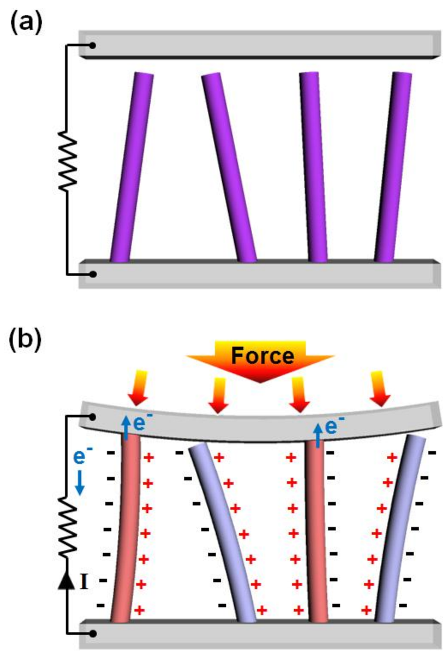

Fig.2. Schematic diagrams showing DC-type output charge generation from T-ZnO nanorods a) before and b) after application of a force.

grown on low seed density layers obtained from the 0.01 M concentration. DC-type output charge generation is based on the coupled effects of semiconducting and piezoelectric properties of ZnO. When ZnO nanorods are subject to an external force, the nanorods are bent and generate piezoelectric potential due to charges induced via the polarization created by ionic charges of lattice ions along the width of the nanorods. A positive potential is produced at the stretched side of the nanorod and a negative potential is induced at the compressed side as shown in Figure 2.

In case that we apply a rigid top electrode on ZnO nanorods, all force directions transferred from the top electrode by a pusing load are normal to the electrode. Thus, for example, right-tilted nanorods should bend toward right-hand direction and left-tilted nanorods bend toward left-hand direction. Based on the previous charge generating mechanism in NGs,[8] DC-type charges then can not be generated from the NGs since compressive sides of bent nanorods can not contact with the top electrode. However, in case of a soft flexible top electrode, the force directions applied by pushing are different. In other words, when we push the flexible top electrode, the electrode is also bent, so that nanorods under the top electrode are actually subjected to forces with various directions. Furthermore, some nanorods can undergo buckling. Thus, right-tilt nanorods can bend toward left-hand direction under left-handed forces, and then TF-NGs can generate DC-type charges by pushing (Fig. 2b).

When the ZnO nanorods are in contact with the flexible top electrode by applying the external force, electrons flow from the compressed sides of the ZnO nanorods to the top electrode.[8] During this process, a Schottky barrier between the ZnO and the electrode plays a critical role in enhancing output performance, since the Schottky barrier accumulates free carriers at the interface.[8,15] This fact indicates that electrode materials with much higher work functions than the electron affinity of ZnO are extremely desirable to fabricate TF-NGs with high output performance.

It is generally expected that Schottky contact formation between ZnO nanorods and ITO is rather weak considering the work function of ITO and the electron affinity of ZnO.[8] However, a Schottky barrier can be substantially changed under an external force due to the change of contact geometry in this work. The weak external force (below 0.1 kgf) leading to slight contact formation between the top ITO electrode and the ZnO nanorods resulted in the observation of the typical rectifying behavior in current-voltage (I-V) measurements (not shown). On the other hand,

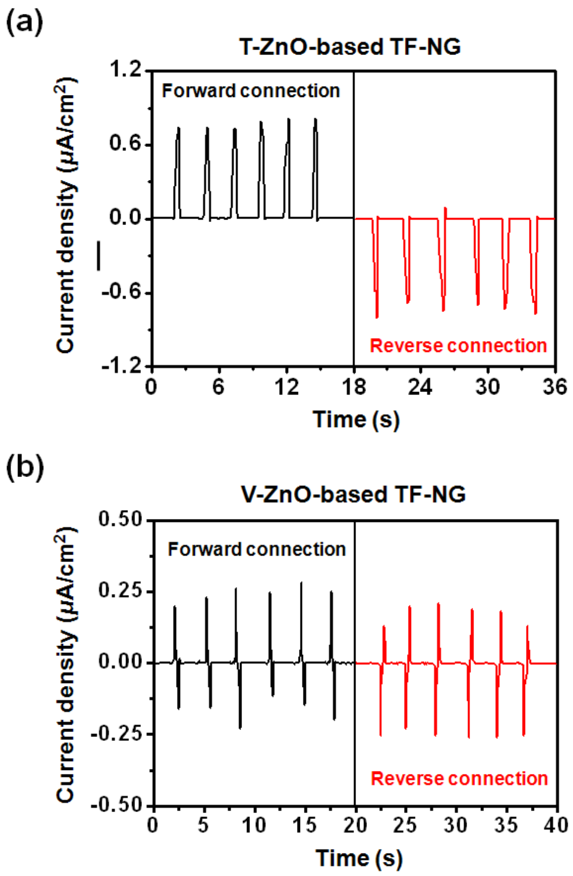

Fig.3. Piezoelectric charge generating behaviors depending on ZnO nanorod morphologies. a) T-ZnO-based TF-NG which shows DC-type charge generation. b) V-ZnO-based TF-NG that presents AC-type charge generation.

the ohmiclike I-V behavior was revealed under the external force above 0.1 kgf. Such an energy barrier leads to resisting the electron flow from the top electrode to the nanorods but allowing electrons to flow from the nanorods to the top electrode. However, we cannot totally rule out the possibility of the electron flow from the compressed sides of the ZnO nanorods to the bottom ITO electrode in part by weak Schottky (ohmiclike) contact formation rather than ohmic contact formation between the nanorods and the bottom ITO electrode.

Figure 3a describes DC-type charge generation from a T-ZnO-based TF-NG. Based on the previously proposed mechanism of charge generation from ZnO nanorods, we attribute the DC-type output signal to the presence of mostly tilted nanorods grown on the low-density seed layer. Since the tilted nanorods are easily bent by an external pushing force (under the load of 0.9 kgf), the piezoelectric potential is formed along the width of the ZnO nanorods. Then, piezo-potential induced charges follow DC-type output behavior along the internal and external circuit of the TF-NG. To verify that the measured signal is from the TF-NG rather than the measurement system, we performed switching-polarity tests,[8-10] as shown in Figure 3a. As the current meter was forward connected to the TF-NG, a positive current pulse was recorded by pushing. When the current meter was reversely connected, the current pulses were also reversed, thus demonstrating that the output signal is generated by our device.

We also measured the electrical current from a V-ZnO-based NG. Interestingly, we found a mainly AC-type output current, as shown in Figure 3b. The AC-type current behavior is attributed to the direct compression of ZnO nanorods by an external force (under the load of 0.9 kgf). Considering the geometry of the V-ZnO, vertically well-aligned nanorods are easily compressed by an external pushing force in the direction of the rod length rather than being bent.[6,8] As-grown ZnO nanorods have a wurtzite structure and a preferred [001] *c*-axis growth direction. Since the crystallographic alignment of the nanorods indicates that their piezoelectric alignment is a response to external stress, a piezoelectric potential is generated into the ZnO nanorod along the *c* axis under uniaxial strain. Therefore, when an external force results in uniaxial strain of V-ZnO nanorods, one side of the nanorods is subjected to a negative piezoelectric potential and the other side becomes a positive potential. [4,6,8]

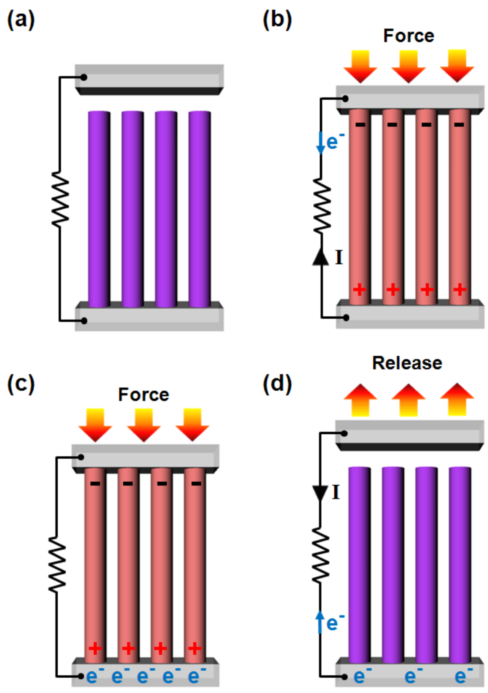

Fig.4. Proposed mechanism for AC-type charge generation in V-ZnO-based TF-NGs. a) The as-received V-ZnO-based TF-NG. b) Electrons flow from the electrode contacting at the sides of nanorods with negative potential to the opposite electrode contacting at the sides of nanorods with positive potential through the external circuit under a compressive force. c) The piezo-potential induced electrons are then moved via the external circuit and are accumulated at the interface between the electrode and the side of nanorods with positive potential. d) As the external force is removed, the piezoelectric potential inside the nanorods instantly disappears and the accumulated electrons flow back via the external circuit.

Depending on the work function of electrodes at the top and the bottom of the TF-NG, the contacts between the electrodes and the nanorods may be of either Schottky or ohmic types. In order to generate a measurable signal above the noise level from TF-NGs, the presence of a Schottky contact at one end of the nanorods is essential because ohmic contacts at both ends lead to no output signal generation. The Schottky contact at the sides of nanorods with negative potential enhances the output signal by preventing electron flow into the ZnO nanorods through the interface (Fig. 4b). The piezo-potential induced electrons are then moved via the external circuit and are accumulated at the interface between an electrode and the side of nanorods with positive potential (Fig. 4c). As the external force is removed and the compressive strain is released, the piezoelectric potential inside the nanorods instantly disappears and the accumulated electrons flow back via the external circuit (Fig. 4d), creating a negative electric pulse, and consequently recoding the current in AC mode for V-ZnO-based TF-NGs. Under the same external force, the strain caused by the direct compression of nanorods is small, compared to that of bending nanorods. Since the output performance of piezoelectric NGs is mainly dependent on the strain of piezoelectric material, the output current density (about 0.8 $\mu A/cm^2$) of a T-ZnO-based TF-NG is higher than that (about 0.25 $\mu A/cm^2$) of a V-ZnO-based TF-NG under the pushing force of 0.9 kgf. Therefore, it can be concluded that the output charge generation mode from TF-NGs under a pushing force is changed between AC type and DC type by the morphological geometry of ZnO nanorods grown on a substrate according to the seed density. Our experimental data support the mechanism that the electric charges can be output by two ways: the electron oscillation in the external load without flowing through the nanorod under the driving of the piezopotential and the presence of a Schottky contact at the top electrode (AC mode)[4,6]; and the electron flow through the nanorod as governed by the Schottky contact (DC mode). [1,8-10,15]

3. Conclusions

We demonstrated that mode control of output power generation in TF-NGs between DC-type and AC-type is based on the morphology of ZnO nanorods grown on different seed densities. We found that tilted ZnO nanorods grown on low-density seed layers generated DC-type piezoelectric charges while vertically aligned ZnO nanorods grown on high-density seed layers exhibited AC-type charge generation.

References

[1] a) Z. L. Wang, J. H. Song, *Science* **2006**, *312*, 242; b) J. H. He, C. L. Hsin, J. Liu, L.-J. Chen, Z. L. Wang, *Adv. Mater*. **2007**, *19*, 781.

[2] J. Liu, P. Fei, J. H. Song, X. D. Wang, C. S. Lao, R. Tummala, Z. L. Wang, *Nano Lett*. **2008**, *8*, 328.

[3] Z. L. Wang, *Adv. Func. Mater*. **2008**, *18*, 3553.

[4] R. Yang, Y. Qin, L. Dai, Z. L. Wang, *Nat. Nanotechnol*. **2009**, *4*, 34.

[5] R. Yang, Y. Qin, C. Li, G. Zhu, Z. L. Wang, *Nano Lett*. **2009**, *9*, 1201.

[6] a) S. Xu, Y. Qin, C. Xu, Y. Wei, R. Yang, Z. L. Wang, *Nat. Nanotechnol*. **2010**, *5*, 366; b) S. N. Cha, J.-S. Seo, S. M. Kim, H. J. Kim, Y. J. Park, S.-W. Kim, J. M. Kim, *Adv. Mater*. **2010**, *22*, 4726.

[7] S. Xu, N. Adiga, S. Ba, T. Dasgupta, C. F. Jeff Wu, Z. L. Wang, *ACS Nano* **2009**, *3*, 1803.

[8] M.-Y. Choi, D. Choi, M.-J. Jin, I. Kim, S.-H. Kim, J.-Y. Choi, S. Y. Lee, J. M. Kim, S.-W. Kim, *Adv. Mater*. **2009**, *21*, 2185.

[9] D. Choi, M.-Y. Choi, H.-J. Shin, S.-M. Yoon, J.-S. Seo, J.-Y. Choi, S. Y. Lee, J. M. Kim, S.-W. Kim, *J. Phys. Chem. C* **2010**, *114*, 1379.

[10] D. Choi, M.-Y. Choi, W. M. Choi, H.-J. Shin, J.-S. Seo, J. Park, S.-M. Yoon, S. J. Chae, Y. H. Lee, S.-W. Kim, J.-Y. Choi, S. Y. Lee, J. M. Kim, *Adv. Mater*. **2010**, *22*, 2187.

[11] S.-D. Lee, Y.-S. Kim, M.-S. Yi, J.-Y. Choi, S.-W. Kim, *J. Phys. Chem. C* **2009**, *113*, 8954.

[12] Y.-J. Lee, T. L. Sounart, D. A. Scrymgeour, J. A. Voigt, J. W. P. Hsu, *J. Cryst. Growth* **2007**, *304*, 80.

[13] M. Wang, C.-H. Ye, Y. Zhang, H.-X. Wang, X.-Y. Zeng, L.-D. Zhang, *J. Mater Sci : Mater Electron* **2008**, *19*, 211.
[14] L. E. Greene, M. Law, D. H. Tan, M. Montano, J. Goldberger, G. Somorjai, P. Yang, *Nano Lett*. **2005**, *5*, 1231.
[15] a) X. D. Wang, J. H. Song, J. Liu, Z. L. Wang, *Science* **2007**, 316, 102; b) C.-T. Huang, J. Song, W.-F. Lee, Y. Ding, Z. Gao, Y. Hao, L.-J. Chen, Z. L. Wang, *J. Am. Chem. Soc*. **2010**, *132*, 4766.