

ZnO Nanogenerator Prepared from ZnO Nanorods Grown by Hydrothermal Method

Chih-Cheng Chen,¹ Tung-Lung Wu,^{2*} Teen-Hang Meen,^{3**}
Chao-Yang Chen,¹ Che-Hsiang Su,³ Jenn-Kai Tsai,³
Chun-Ying Lee,⁴ Chun-Hsien Lee,⁴ and Day-Shan Liu⁴

¹School of Information Engineering, Jimei University, Xiamen, Fujian 361021, China

²School of Mechanical and Automotive Engineering, Zhaoqing University, Zhaoqing, Guangdong 516260, China

³Department of Electronic Engineering, National Formosa University, Huwei, Yunlin 632, Taiwan

⁴Institute of Electro-Optical and Materials Science, National Formosa University, Huwei, Yunlin 632, Taiwan

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In this study, a zinc oxide (ZnO) film was deposited by sputtering on an indium tin oxide (ITO) glass substrate. ZnO nanorods were then grown on the film by the hydrothermal method, then assembled with a gold electrode to fabricate a nanogenerator. The ZnO nanostructure and nanogenerator were analyzed by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and the measurement of current–voltage characteristics. The results of FE-SEM show that the length of the ZnO nanorods increased with the growth time, and the optimal dimensions of the ZnO nanorods were a length of 2 μm and a diameter of 130 nm at the growth time of 6 h. In the XRD pattern, ZnO (002) and (103) peaks were observed at $2\theta = 34.45$ and 62.51° , respectively, confirming that the ZnO nanorods were grown on the substrate. The nanogenerator was driven by an ultrasonic wave to measure its voltage and current. The highest average current and voltage were 3.46×10^{-6} A and 5.63×10^{-2} V, respectively. These results indicate that the ZnO nanorods prepared by the hydrothermal method are suitable for the fabrication of a nanogenerator.

1. Introduction

Zinc oxide (ZnO) is a II-VI semiconductor material with a direct band gap of 3.37 eV, corresponding to a wavelength in the ultraviolet region, and it also has a large excitation binding energy (~ 60 meV). In addition, ZnO has low resistivity and high transparency; therefore, it is considered as a promising material for application in optoelectronics. Recently, ZnO materials with the characteristics of one-dimensional (1D) nanomaterials have been realized, which can exhibit different nanostructures depending on the fabrication method of the materials. Over the past ten years, the synthesis of ZnO nanostructures such as nanowires, nanocycles, nanobelts, and nanocombs has been successfully achieved. The most representative structure is nanowires.

*Corresponding author: e-mail: tunglung216@gmail.com

**Corresponding author: e-mail: thmeen@nfu.edu.tw

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Nanotechnology involves the use of nanomaterials with various dimensions to assemble the desired structure. Nanostructures such as quantum dots and quantum wells can be used for illumination or metering. ZnO nanomaterials not only can be used for the basic theoretical study of physical properties, such as light, electricity, magnetism, and mechanics, but also have great potential as nanooptical components, such as light-emitting diodes (LEDs),⁽¹⁾ field emission elements,⁽²⁾ surface coatings of conductive materials,⁽³⁾ laser diodes,^(4–6) solar cells, gas sensors, photonic crystals, field-effect transistors (FETs), and photodetectors.⁽⁷⁾ In addition, ZnO is also a piezoelectric semiconductor material when prepared as a film. Some types of ZnO film can be applied to a surface acoustic wave (SAW) device. When ZnO is prepared in a 1D form, it can be used as a nanogenerator.^(8–10) In this study, a ZnO film was deposited by sputtering on an indium tin oxide (ITO) glass substrate, then ZnO nanorods were on the film grown by the hydrothermal method to fabricate a nanogenerator. The characteristics of the ZnO nanorods and nanogenerator were investigated by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and current–voltage measurements, and the results reveal that a ZnO nanogenerator can be fabricated successfully by this low-cost hydrothermal method.

2. Experimental Procedure

A ZnO thin film was prepared by sputtering the ZnO target (3 inch, 99.9%) onto an ITO glass substrate as a seed layer. The thickness of the ZnO seed layer was 500 nm. ZnO nanorods were grown on the seed layer in zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2$, 0.03 M] and hexamethylenetetramine (HMTA, 0.03 M) for 3, 6, 9, or 12 h at 90 °C by the hydrothermal method, and then the grown ZnO nanorods were removed from the solution, rinsed with distilled water, and dried in air. The surface morphology of the ZnO nanorods was observed by FE-SEM. The crystallinity of the ZnO nanorods was analyzed by XRD. To assemble the nanogenerator, a gold film was deposited on the etched ITO glass substrate as an electrode. The microcurrent of the nanogenerator was measured in DI water by driving ultrasonic waves with a frequency of 42 kHz and exhibited a power of 100 W. The ZnO nanogenerator generated an output current and demonstrated a Schottky-like current–voltage characteristic.

3. Results and Discussion

Nanorods with four different lengths and widths were grown on the seed layer for 3, 6, 9, and 12 h at 90 °C by the hydrothermal method. Figure 1 shows top-view and cross-sectional SEM images of the ZnO nanorods. The lengths of the ZnO nanorods grown on the seed layer for 3, 6, 9, and 12 h were 800 nm, 2 μm , 2 μm , and 2 μm and the widths were 80, 130, 150, and 170 nm, respectively. These results reveal that the length and width of the ZnO nanorods increase with the growth time, and the length of the ZnO nanorods hardly changes when the growth time is longer than 6 h. Figure 2 shows the energy-dispersive X-ray spectroscopy (EDS) spectrum of the ZnO nanorods grown for 6 h. The result indicates that the atomic ratio of Zn to O is nearly 1, and there are other elements in the ZnO nanorods.

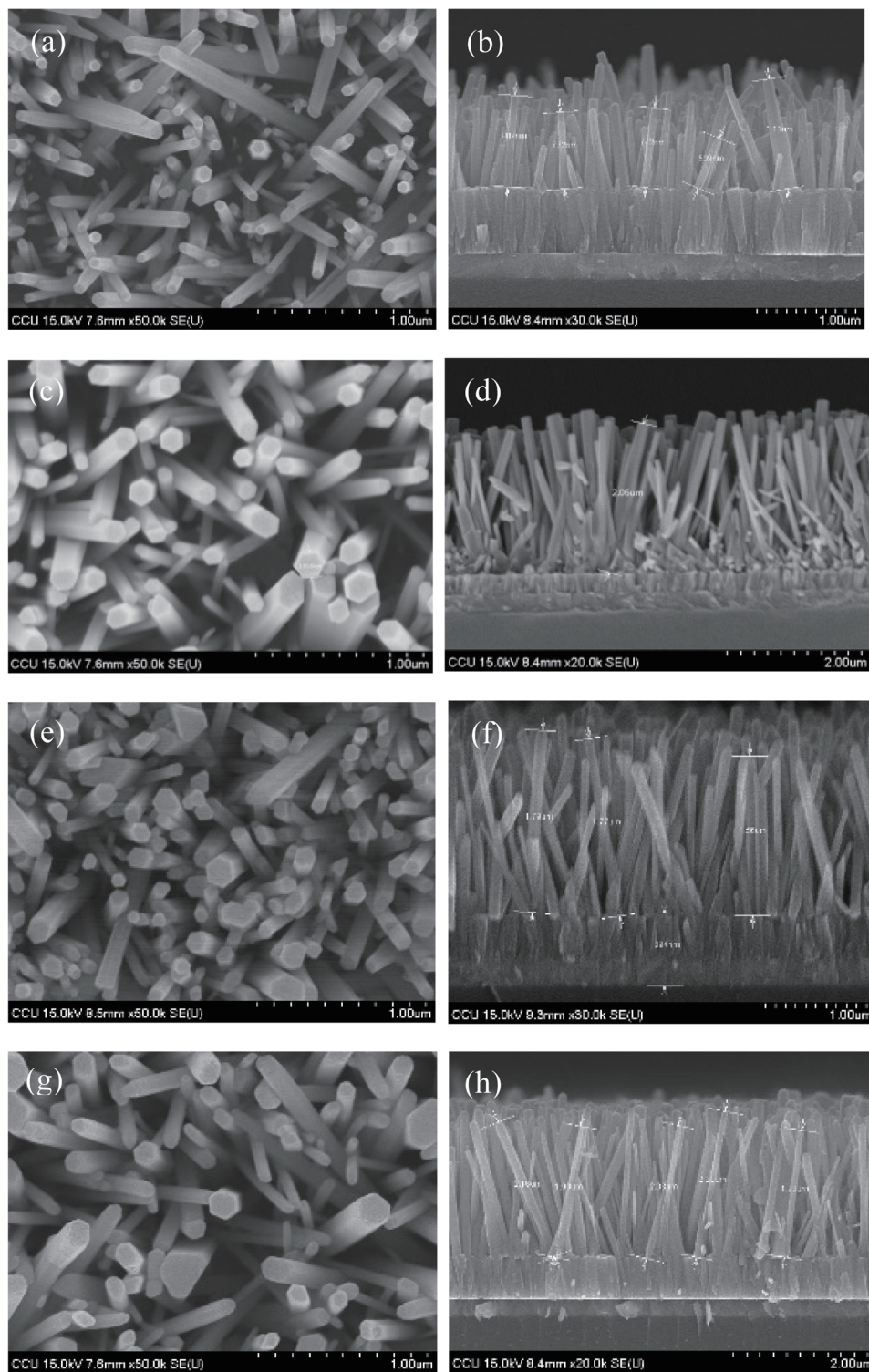


Fig. 1. Top-view and cross-sectional SEM images of ZnO nanorods for growth times of (a, b) 3, (c, d) 6, (e, f) 9, and (g, h) 12 h.

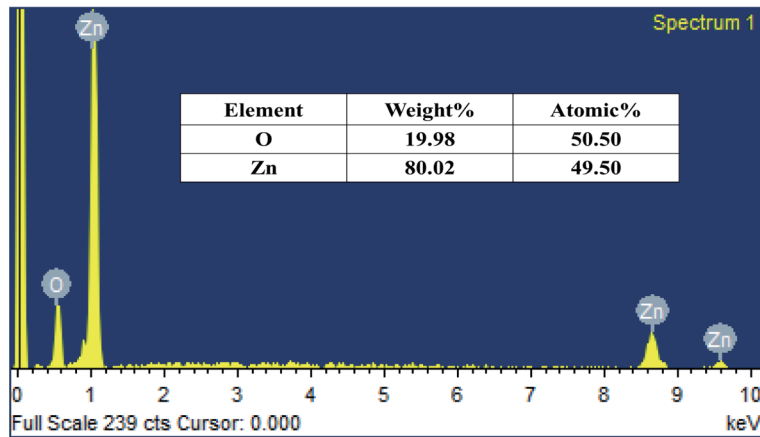


Fig. 2. (Color online) EDS spectrum of the ZnO nanorods grown for 6 h.

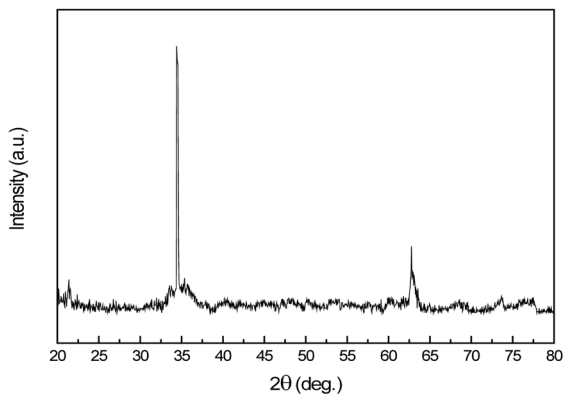


Fig. 3. XRD pattern of the ZnO nanorods grown for 6 h.

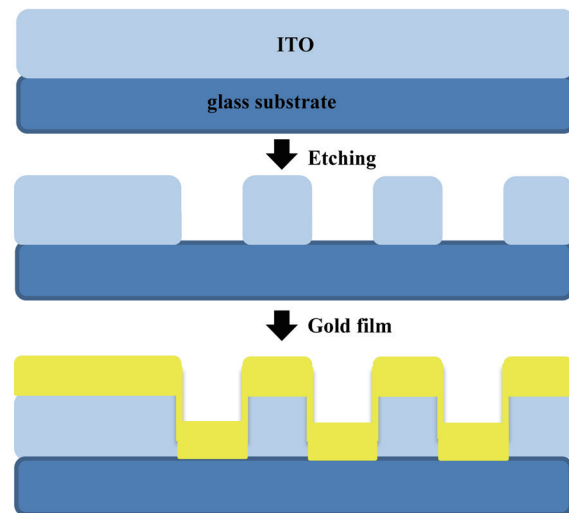


Fig. 4. (Color online) Diagram of deposition of gold electrode on ITO glass substrate.

Figure 3 shows the XRD pattern of the ZnO nanorods grown for 6 h. As shown in Fig. 3, a strong ZnO (002) diffraction peak was observed at $2\theta = 34.45^\circ$. It indicates that the ZnO nanorods on the substrate are mainly oriented along the c-axis. In addition, a (103) peak also appears since not all the ZnO nanorods have c-axis orientation and some of them are skewed.

To assemble the nanogenerator, a gold film was deposited on the etched ITO glass substrate as an electrode. After cleaning the substrate with acetone, isopropanol, and DI water, the etched ITO glass was placed in the oven to dry. The gold film was coated by evaporation, and its thickness was about 100 nm. Figure 4 shows a diagram of the deposition of the gold electrode on the ITO glass substrate.

Figures 5–7 show the current voltage characteristics of the ZnO nanogenerators fabricated by ZnO nanorods grown for 3, 6, and 9 h, respectively. The nanogenerators were driven by a fluctuation generated with an ultrasonic oscillator. The current voltage characteristics show Schottky contact behavior between the metal and the oxide layer, and the average currents and voltages are 9.52×10^{-8} A and 7.04×10^{-2} V for 3 h, 3.46×10^{-6} A and 5.63×10^{-2} V for 6 h, and 4.75×10^{-7} A and 3.38×10^{-2} V for 9 h, respectively, and the output powers are 6.7×10^{-9} W for 3 h, 1.95×10^{-7} W for 6 h, and 1.6×10^{-8} W for 9 h. From the viewpoint of the total power, the best nanogenerator is fabricated with the ZnO nanorods grown for 6 h. Note that because thinner ZnO nanorods can be bent more easily, they can generate more output power than the thicker ZnO nanorods. From Fig. 1, the lengths of the ZnO nanorods grown for 3, 6, and 9 h are 800 nm, 2 μ m, and 2 μ m and the widths are 80, 130, and 150 nm, respectively. Because the length of the ZnO nanorods hardly changes after 6 h, the optimal ZnO nanogenerator is fabricated with ZnO nanorods grown for 6 h. This may also be due to the ZnO nanorods grown for 6 h having a suitable length of 2 μ m while having a smaller diameter than the ZnO nanorods grown for 9 h, resulting in the highest output power when driven by the fluctuation generated by the ultrasonic oscillator.

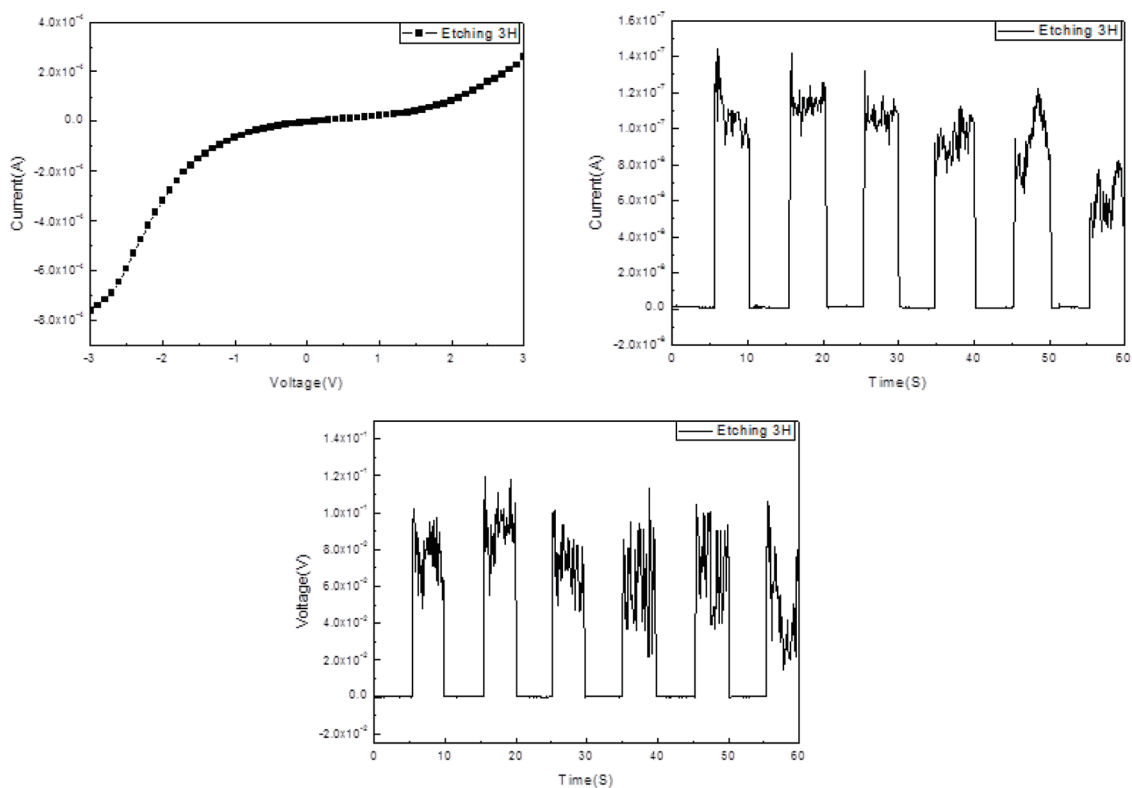


Fig. 5. Current–voltage characteristics of the ZnO nanogenerator fabricated from ZnO nanorods grown for 3 h.

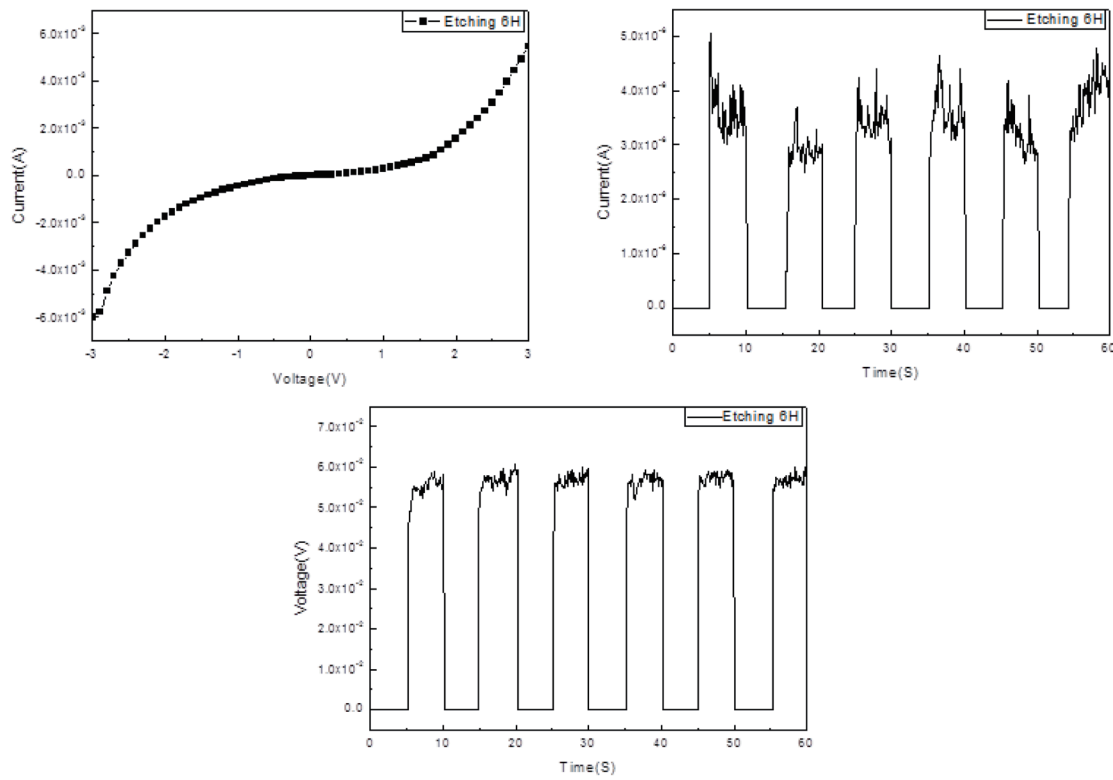


Fig. 6. Current–voltage characteristics of the ZnO nanogenerator fabricated from ZnO nanorods grown for 6 h.

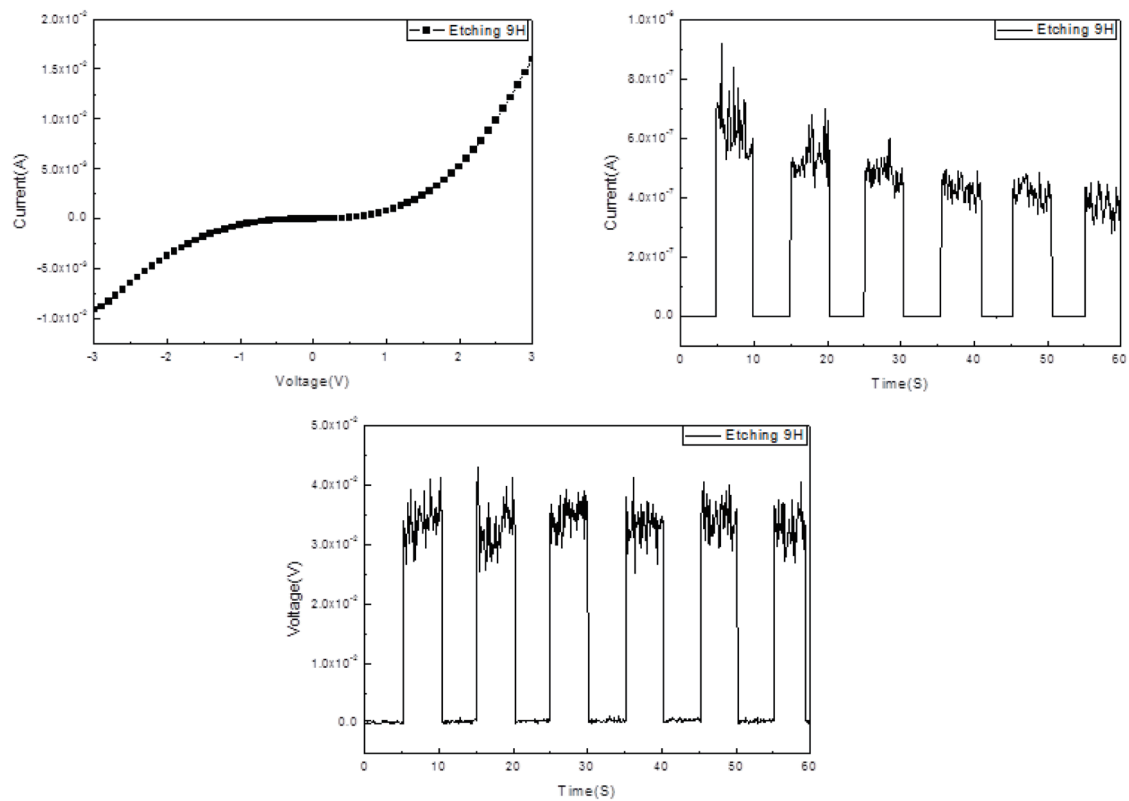


Fig. 7. Current–voltage characteristics of the ZnO nanogenerator fabricated from ZnO nanorods grown for 9 h.

4. Conclusions

In this study, a ZnO nanogenerator was fabricated from ZnO nanorods grown by the hydrothermal method. The optimal growth time of the ZnO nanorods was 6 h. The highest average current and voltage were 3.46×10^{-6} A and 5.63×10^{-2} V, respectively. These results demonstrate that ZnO nanorods prepared by the hydrothermal method can be used to fabricate a nanogenerator.

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