Synthesis of Ga-Doped ZnO Nanorods Using an Aqueous Solution Method for a Piezoelectric Nanogenerator

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Mechanical energy is a potential energy source for self-powered electronic devices. Due to their unique semiconducting and piezoelectric properties, wurtzite-structured nanomaterials have been considered as potential candidates for piezoelectric nanogenerators that convert mechanical energy into electricity. In the present work, we report on the growth of Ga-doped ZnO (GZO) nanorods and investigate the performance of nanogenerators fabricated from undoped ZnO (UZO) nanorods, low Ga-doped ZnO (LGZO) nanorods, and high Ga-doped ZnO (HGZO) nanorods. A nanogenerator integrated with LGZO nanorods exhibited a current density of 1.2 μA/cm², an enhancement over the 0.4 μA/cm² and 0.7 μA/cm² current densities of nanogenerators integrated with UZO and HGZO nanorods, respectively.

Keywords: ZnO, Gallium-Doping, Nanogenerator, Current Density.

1. INTRODUCTION

Energy shortage has long been a concern of the international community. In addition, fossil fuels reserves are limited, and their usage increases the amounts of CO₂ and other gases in the atmosphere, which in turn causes global warming. As such, there is a need for the development of clean and environmentally-friendly alternative energy sources.¹,² In recent years, researchers have devoted a great deal of effort to the study of solar cells,³,⁴ fuel cells,⁵,⁶ thermoelectric,⁷ and piezoelectric technologies⁸,⁹ because of their potentials for converting photon, chemical, thermal and mechanical energies into electrical energy. Among these technologies, piezoelectric energy harvesting is an eco-friendly energy-converting system in which waste mechanical energy, such as tiny vibrations or the movement of the human body, is converted into electricity.¹⁰ These small and lightweight energy-converting devices have unique advantages such as a simple structure and a high energy conversion efficiency.⁹,¹⁰ Recently, the piezoelectric properties of several materials such as zinc oxide (ZnO),⁶,¹² lead zirconate titanate,¹³ cadmium sulfide,¹⁴ barium titanate,¹⁵ and gallium nitride¹⁶ have been successfully demonstrated.

Researchers have attempted to improve the piezoelectric output performances of materials for use in the operation of self-powered nanodevices. There are several significant factors that must be considered to improve the performance of piezoelectric nanogenerators. One of the most important of these is increased carrier density. It has been found that the carrier density arising from ultraviolet irradiation effects the output currents of nanogenerators.¹⁷,¹⁸ However, the n-type doping effect on the performances of direct current (DC)-mode nanogenerators has rarely been studied. ZnO is usually doped with group III elements such as B,¹⁹ In,²⁰ Al,²¹ and Ga.²²-²⁴ Among these elements, Ga is an especially promising n-type dopant for low resistivity ZnO films with high transmittance in the visible range.²²-²⁴ In Ga doping, Zn ions in the ZnO lattice are replaced by Ga atoms, which act as a substitution impurity. In this process, a free electron is released in the conduction band at room temperature. The ionic and covalent radii (0.62 and 1.26 Å, respectively) of Ga are similar to those of Zn (0.74 and 1.34 Å). As a result, only a small lattice deformation occurs at high Ga-doping concentrations.²³,²⁴

In this paper, we report on the growth of Ga-doped ZnO (GZO) nanorods and investigate the performances of nanogenerators fabricated from undoped ZnO (UZO) nanorods and GZO nanorods with various Ga dopant concentrations. We were ultimately able to determine the proper amount of Ga dopant in the ZnO nanorods for maximum performance.
2. EXPERIMENTAL DETAILS

In order to grow UZO and GZO nanorods, a ZnO buffer layer with a thickness of about 50 nm was initially deposited onto indium tin oxide (ITO)/polyethersulfone (PES) substrates via radio frequency sputtering. The ZnO nanorods were then grown using the hydrothermal method. In this process, an aqueous solution was first prepared with 25 mM zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), 25 mM hexamethylenetetramine (C$_6$H$_{12}$N$_4$), and different amounts of gallium nitrate (0 wt%, 1 wt%, and 10 wt% of the zinc nitrate hexahydrate). The substrates with a ZnO buffer layer were then placed into this solution at 95 °C for 3 h. A PES substrate onto which gold (Au), deposited via thermal evaporation, was used as the top electrode of the structure in order to ensure Schottky contact with the ZnO nanorods. The size and morphology of the ZnO nanorods were characterized using field emission scanning electron microscopy (FE-SEM). X-ray diffraction (XRD) measurements were used to confirm the crystal growth quality and the Ga doping of the ZnO nanorods. X-ray photoelectron spectroscopy (XPS) was employed to confirm the relative Ga doping concentration in the ZnO nanorods. A Keithley 6485 picoammeter was used for low-noise current measurements in order to detect the current generated by the piezoelectric nanodevices.

3. RESULTS AND DISCUSSION

FE-SEM images of the typical surface morphologies of UZO nanorods, low (gallium nitrate at 1 wt% of the zinc nitrate hexahydrate concentration) Ga-doped ZnO (LGZO) nanorods, and high (gallium nitrate at 10 wt% of the zinc nitrate hexahydrate concentration) Ga-doped ZnO (HGZO) nanorods grown on ITO/PES substrates are shown in Figure 1. As the Ga dopant concentration increased, the nanorod density remained fairly constant, while the average diameter of the nanorods decreased slightly. The diameters of the UZO, LGZO, and HGZO nanorods were 110 nm (Fig. 1(a)), 85 nm (Fig. 1(b)), and 75 nm (Fig. 1(c)), respectively. Due to the difference in the radii of Zn and Ga, rapid growth occurred in the (002) direction. Doping with Ga can support the growth of ZnO in this direction.\(^2\)\(^2\)\(^5\)

The diffraction patterns of the UZO and GZO nanorods from a synchrotron X-ray source are shown in Figure 2(a). The scans were taken along the surface normal direction, \(Q = 4\pi \sin(\Theta/2)/\lambda\), in reciprocal space. The peak positions at \(Q\) values of 2.413 Å$^{-1}$ and 2.229 Å$^{-1}$ were assigned to the (002) and (100) planes, respectively, of the ZnO nanorods. The XRD spectra revealed that GZO was formed in the c-axis direction.\(^2\)\(^6\) Since Ga doping was employed, the intensity of the (002) peak decreased, and the full width at half maximum (FWHM) remained constant for the LGZO nanorods and slightly increased from 0.005 Å$^{-1}$ to 0.006 Å$^{-1}$ for the HGZO nanorods. It was found that a low amount of Ga doping did not deteriorate the crystallinity of the GZO. In the XRD spectra, no Ga$_2$O$_3$ peak was detected. The absence of this peak indicates that Ga atoms successfully replaced Zn sites in the lattice. The XPS data confirmed the presence of Ga dopant in the GZO nanorods, as shown in Figure 2(b). The peaks at 1116.94 eV and 1143.95 eV are attributed to the electronic states of Ga 2p$_{3/2}$ and Ga 2p$_{1/2}$, respectively. The energy gap of 27.01 eV is consistent with the value of Ga in LGZO and HGZO nanorods,\(^2\)\(^2\) while no peak related to Ga was detected in the UZO nanorods. The higher Ga doping of 10 wt% was confirmed by the relatively higher magnitudes of the Ga 2p$_{3/2}$ and Ga 2p$_{1/2}$ peaks compared to those obtained at the lower Ga doping concentration.
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To investigate the effect of Ga doping on the current-generating performance of piezoelectric nanogenerators with external force applied, we fabricated a series of nanogenerator devices from UZO nanorods and GZO nanorods with different amounts of Ga. A schematic of the nanogenerators integrated with piezoelectric UZO nanorods and GZO nanorods grown on ITO/PES substrates with an Au/PES top electrode is shown in Figure 3(a).

To confirm that the measured signal originated from the device, a switching polarity test of the induced output current density was performed, as shown in Figure 3(b). When the current meter was forward connected to a UZO- or GZO-based nanogenerator, we measured a positive signal of the current pulse during pushing. When the current meter was reversely connected, the negative signal of the current pulses was recorded. The measured signals of the current density for both connection conditions were almost the same. Typically, this signal looks like the DC mode of a generator. However, we repeatedly detected a very small signal in the opposite direction as the reference point. As shown in Figure 1, this is due to the existence of a few nanorods that were vertically grown on the substrate. These nanorods acted as a potential gate to repulse electrons from the top electrode to the bottom electrode. The electrons then returned to the top electrode.

We compared the induced current density performance of different piezoelectric nanogenerators by applying the same pushing force to the top electrode of the nanodevices in the vertical direction. Compared to the nanogenerators integrated with UZO nanorods (Fig. 3(b)) or HGZO nanorods (Fig. 4(b)), the nanogenerator integrated with LGZO nanorods showed enhanced performance (Fig. 4(a)). At a load of 0.5 kgf, the nanogenerators with UZO, LGZO, and HGZO nanorods had average current densities of 0.4 µA/cm², 1.2 µA/cm², and 0.7 µA/cm², respectively. The extent of Ga doping and the free electron density were also found to affect the current-generating performance. With a large number of free electron carriers or defects in the ZnO nanorods, the charge of the piezoelectric would be screened, and the amplitude of the piezoelectric potential would be decreased. This

Fig. 2. (a) XRD data for UZO, LGZO, and HGZO nanorods using a synchrotron X-ray source. (b) XPS results showing Ga 2p$_{3/2}$ and Ga 2p$_{1/2}$ peaks obtained from LGZO and HGZO nanorods.

Fig. 3. (a) Schematic of an integrated nanogenerator. (b) Current densities from the UZO nanorod-based piezoelectric nanodevice (switching polarity test).

Fig. 4. Output current density from (a) the LGZO-based nanogenerator and (b) the HGZO-based nanogenerator.
would result in a reduction in the output current density. However, if the free electron carrier density was very low in the ZnO nanorods, even though the local piezoelectric potential could increase, the output current would decrease because a lower number of free carriers transferred from the ZnO to the top Au electrode during Schottky junction formation. Hence, an optimum free electron carrier density in ZnO is required to optimize the generator for the highest output.  

4. CONCLUSION

The obtained experimental results reveal that a small amount of Ga dopant in ZnO supplies an optimum concentration of free electron carriers to enhance the piezoelectric output current. However, a larger amount of Ga dopant reduces the output current of the nanogenerator due to a slight deterioration in the crystallinity of the HGZO nanorods, where defects act as trapping sites for carriers and the piezoelectric potential. Such a scenario is evident in the XRD patterns, where the FWHM increased for increased Ga doping in ZnO. The present work suggests that the amount of gallium dopant is an important issue to consider when maximizing the performance of a nanogenerator. Through variation of the Ga dopant concentration, we optimized the performances of nanogenerators fabricated with Ga-doped ZnO nanorods.

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References and Notes


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