

Article

Synthesis of Ga-Doped ZnO Nanorods by Hydrothermal Method and Their Application to Ultraviolet Photodetector

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Abstract: In this study, high-density single crystalline Ga-doped ZnO (GZO) nanorods were grown on glass substrate by the hydrothermal method. The structural and optoelectronic properties of Ga-doped ZnO nanorods were studied. The microstructure of the GZO was studied by scanning electrical microscope (SEM). The structural characteristics of the GZO were measured by X-ray diffraction (XRD). It was found that the peaks related to the wurtzite structure ZnO (100), (002), and (101) diffraction peaks. The (002) peak indicates that the nanorods were preferentially oriented in the c-axis direction. The existence of Ga was examined by energy diffraction spectra (EDS), indicating the Ga atom entered into the ZnO lattice. The optical properties of the GZO were measured by photoluminescence spectra. It was found that all GZO nanorod arrays showed two different emissions, including UV (ultraviolet) and green emissions. GZO nanorod metal-semiconductor-metal (MSM) ultraviolet (UV) photodetectors (PD) were also fabricated. The photo-current and dark-current constant ratio of the fabricated PD was approximately 15.2 when biased at 1 V.

Keywords: Ga doped ZnO nanorod; hydrothermal; photodetector

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1. Introduction

ZnO has several favorable properties, such as a wide bandgap (3.37 eV) and a large exciton-binding energy (60 meV). Forms of ZnO with wurtzite structures have various morphologies such as nanowires, nanorods, nanotubes, and nanobelts [1–5]. ZnO nanorods are doped with various elements to alter their structural, electrical, and optical characteristics. Al, Ga, and In (group III) elements are used as dopants in the fabrication of n-type ZnO nanorods. Ga is an excellent dopant with high conductivity and low reactivity. As the covalent bond length of Ga–O, 1.92 Å is very close to that of Zn–O, which is 1.97 Å, and Ga-doped ZnO exhibits increased electron mobility and reduced electrical resistivity [6].

Various chemical, electrochemical, and physical deposition techniques have created structures of oriented ZnO nanorod arrays so far. For instance, metal–organic chemical vapor deposition [7], a vapor–liquid–solid epitaxial mechanism [8], pulsed laser deposition [9], spray pyrolysis [10], epitaxial electrodeposition [11], and radiofrequency magnetron sputtering [12] have been successful in creating highly oriented ZnO nanorods. The hydrothermal method is a simple low-temperature method for wet

chemistry and thus has become a promising approach for the large-scale production of nanomaterials. Ya-Ping Hsieh *et al.* [13] synthesized a ZnO nanorod/Si nanotip with the pulsed laser deposition system. Huihu Wang *et al.* [14] synthesized Ga-doped ZnO nanorods with the hydrothermal method. Additionally, the method can directly obtain a product that has high crystallinity as well as excellent conductive properties without sintering. However, many of these demand reaction conditions such as high temperatures and low or high pressures, which go against the large-scale production of this material. Besides, there are also many advantages of ZnO nanorods grown on a glass substrate, such as low cost, greater transparency than the Si substrate, *etc.* Solution chemical processes greatly facilitate the fabrication of large-scale aligned ZnO nanorods with relatively low cost at remarkably low temperatures.

2. Materials and Methods

Initially, our glass substrate used RCA clean method (*i.e.*, the RCA clean is a standard set of wafer cleaning steps) to clean residue, after that a 100-nm-thick ZnO seed layer was deposited on glass by radio frequency magnetron sputtering. Subsequently, a 50-nm-thick Au film was thermally evaporated through an interdigitated shadow mask onto the ZnO seed layer to form contact electrodes. The Ga-doped ZnO (GZO) nanorods were grown by hydrothermal method at 90 °C for 6 h. The synthesis solution was fabricated from zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hexamethylenetetramine and gallium nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), and mixed aqueous solution. Finally, the GZO nanorod substrate was washed with deionized water. Figure 1 show a schematic diagram of the fabricated the GZO nanorod photodetector.

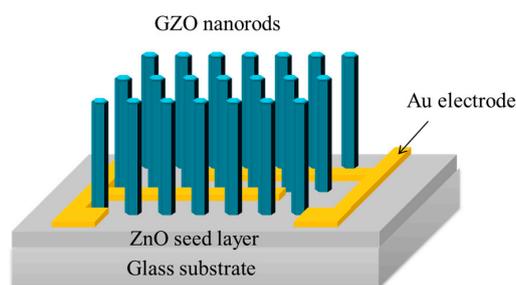


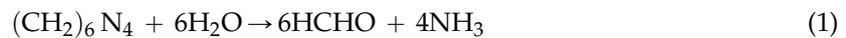
Figure 1. Schematic diagram of the fabricated GZO nanorod photodetector. The GZO nanorods are grown by hydrothermal method.

The surface morphologies and crystal quality of the synthesized materials were characterized using a high-resolution scanning electron microscope (Hitachi S-4800I, Hitachi High-Technologies corporation, Tokyo, Japan) and a high-resolution transmission electron microscope (HRTEM, Philips Tecnai F20 G2 FEG-TEM, Philips, Eindhoven, the Netherlands). X-ray diffractometer (XRD, Bruker D8 advance, Bruker, Germany) was used to characterize the crystallographic and structural properties of the grown GZO nanorods. The optical property of the samples were analyzed by a photoluminescence (PL) measurement system which was made at RT using a He-Cd laser (325 nm, 5 mW) as the excitation light source. A Keithley 2410 semiconductor parameter analyzer was then used to measure the I-V and photodetector characteristic of the fabricated device. The spectral responsivity of the photodetector was measured using a Jobin Yvon-Spex system with a 300 W xenon arc lamp light source (Perkin Elmer PE300BUV, PerkinElmer, Foster City, CA, USA) and a standard synchronous detection scheme measured at 300 Hz.

3. Results and Discussion

Figure 2a,b show GZO nanorods have a well-aligned shape in the vertical direction as seen in the top-view and cross-section SEM image. Figure 2a indicates that the average diameters of the GZO were

around 54 and 49 nm, and Figure 2b shows that average lengths were 1.96 and 1.28 μm , respectively. According to a previous report, the growth mechanism that explains this chemical reaction is as follows:



During this synthesis, $\text{Zn}(\text{NO}_3)_2$ and HMTA serve as a Zn^{2+} ion source and a pH buffer, respectively. The latter keeps the pH values ~ 7 . Hence, the formation of more surface defects at a lower pH is caused by the presence of more H^+ ions, which absorb more OH groups and O^{2-} ions [14–17].

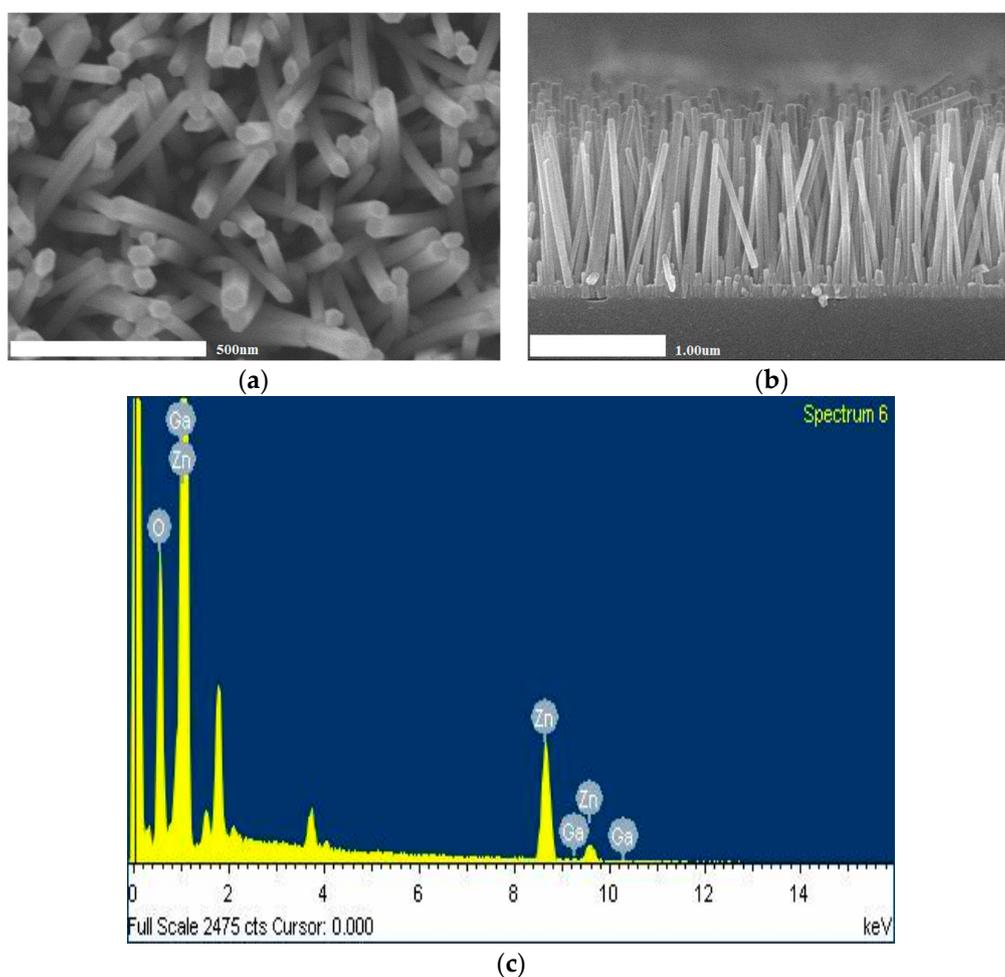


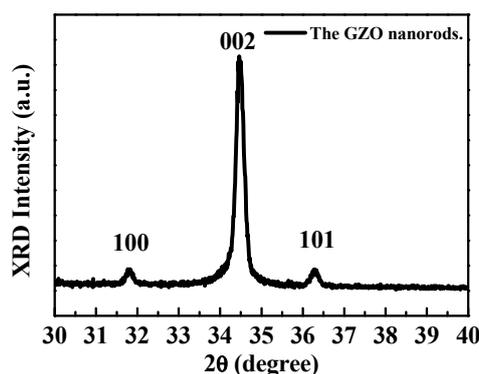
Figure 2. This figure shows GZO nanorods have a well-aligned shape in the vertical direction as seen in the top-view (a) and cross-section (b) SEM image. (c) shows that the existence of Ga was examined by energy diffraction spectra.

Figure 2c shows that the existence of Ga was examined by energy diffraction spectra (EDS), indicating that the Ga atom entered into the ZnO lattice. It is found that the GZO contains 40.11% zinc, 56.33% oxygen and 3.57% gallium as shown in Table 1. The composition ratio of the nanorods is $\text{Ga}_{0.008}\text{Zn}_{0.992}\text{O}$ which agrees well with the desired composition ratio. From the EDS, we see that no other element exists.

Table 1. Shows the GZO nanorods contain zinc, oxygen and gallium, respectively.

Element	EDS		
	O k	Zn L	Ga L
Ga-doped ZnO	56.33%	40.11%	3.57%

Figure 3 shows the structural characteristics of the GZO nanorods were measured by X-ray diffraction (XRD). It was found that the peaks related to the wurtzite structure ZnO (100), (002), and (101) diffraction peaks. The (002) peak indicates that the nanorods were preferentially oriented in the c-axis direction.

**Figure 3.** The XRD pattern of the GZO nanorods.

At room temperature, Figure 4 shows the optical properties of the GZO were measured by photoluminescence spectra. It was found that the GZO nanorod arrays exhibit two different emissions, including UV (ultraviolet) and green emissions. There is a reduction in the UV peak with Ga-doping because Ga atoms enter into the lattice sites, substituting for Zn atoms, causing serious lattice distortions and leading to decreased UV emission peaks. The green emission peak at 560 nm was attributed to the existence of oxygen vacancy and interstitial in our GZO nanorods.

According to previous works, the morphology of GZO nanorods will be converted into a nanosheet along with gallium-doped concentration increases. The crystal structure of GZO nanorods indicated a reduced crystallite quality of the ZnO nanorods (NRs) due to the incorporation of Ga atoms into the ZnO lattice network [17–19], and our PL spectra results are in agreement with previous reports suggesting that Ga doping improves the optical properties of ZnO NR arrays [14,20].

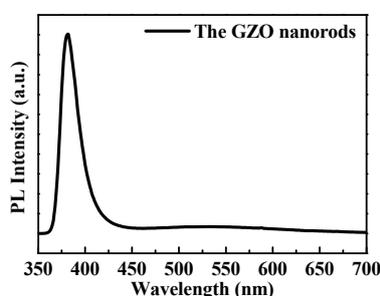
**Figure 4.** Room-temperature PL spectra of GZO nanorods.

Figure 5 shows the photocurrent rise and decay by turning the UV illumination at 365 nm on and off in the air. Before the UV illumination turned on, O₂ molecules adsorbed on the surface of GZO nanorods and formed O₂⁻ by capturing the free electrons of the nanorods. Hence, the phenomenon

decreases not only the carrier density but also the mobility of the remaining carriers by creating depletion layers near the surface [21,22]. When UV illumination is turned on, the photocurrent rapidly increases a huge number of electric-charge pairs. It can be attributed to the holes migrating to the surface to return O_2 by desorbing the O_2^- under UV illumination. After UV illumination is removed, the dark currents decrease by recombining electron-hole pairs [14].

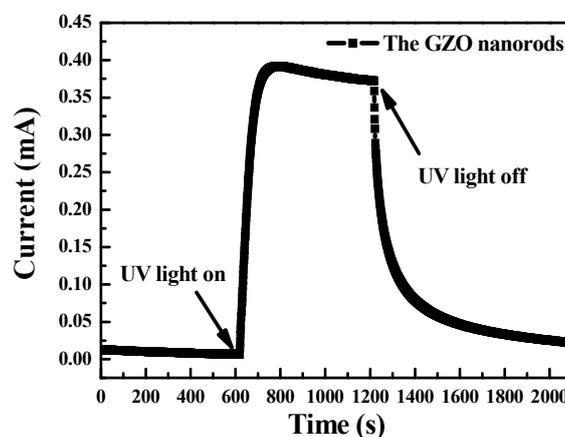


Figure 5. GZO nanorod current-time characteristics at UV illumination.

Under UV illumination at 365 nm in the air at an applied bias of 1 V, the dark current and photocurrent of the GZO nanorod photodetector were 3.8×10^{-4} and 2.5×10^{-5} A, respectively. The photocurrent-to-dark-current contrast ratio of the fabricated photodetector exceeded 15.2.

4. Conclusions

In summary, GZO nanorods were grown on a glass substrate by using a low-temperature hydrothermal method. The GZO nanorods exhibited wurtzite structures. The dynamic response of the GZO nanorod photodetector with Au electrodes had a photo current and dark current of 3.8×10^{-4} and 2.5×10^{-5} A, respectively. The photocurrent-to-dark-current contrast ratio of the fabricated photodetector exceeded 15.2.

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Author Contributions: Sheng-Jouue Young conceived and designed the experiments; Chia-Lin Chiou and Yi-Hsing Liu performed the experiments; Liang-Wen Ji participated in data analysis. All authors read and approved the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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