Materials Science in Semiconductor Processing 64 (2017) 101–108

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

# Surface treatment for Schottky barrier photodetector based on Au/GaZnO nanorods/Au structure

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ARTICLE INFO

*Keywords:*
Ga doping
UV photodetector
Surface treatment
Schottky barrier

ABSTRACT

In this paper, we will report the geometrical morphology, optical properties, electrical properties of the gallium doped ZnO nanorods (GZO NRs), as well as the performance of Au/GZO NRs/Au structure photodetector. We found that with the increase of the molar ratio of gallium, the length of the nanorods becomes smaller and the radial width increases, and the shape is more toward the hexagonal prism, and the grain radius increases. Also with the increase of the doping ratio, the optical absorption edge had a blueshift phenomenon, and the conductivity is enhanced. Moreover, in order to obtain the high performance of the photodetector, GZO NRs were treated by hydrogen peroxide and ohmic contact Au/GaZnO Nanorods/Au device was changed to a Schottky contact device, which showed a smaller dark current and faster response speed compared with ohmic contact device.

## 1. Introduction

In recent years, owing to its wide direct band gap (3.37 eV) at room temperature and large exciton binding energy (60 meV), one-dimensional (1D) ZnO nanostructures, such as nanowires, nanorods and nanotubes, are widely used as the basic functional material in the electronic and optoelectronic devices [1–3]. ZnO is a kind of natural n-type semiconductor because of its own defects, such as O/Zn vacancies, O/Zn clearance and some other defects, which lead to the excitation light wavelength in the band of visible light [4,5]. In order to meet the special needs of some short wavelength optoelectronic devices, especially the ultraviolet laser, it is necessary to prepare a high quality doped 1D nanostructure which can enhance the ultraviolet emission and own low impedance. It is well known that highly conductive *n*-type ZnO have been achieved by replacing $Zn^{2+}$ ions by other ions (acting as efficient donors) such as $In^{3+}$, $Al^{3+}$ and $Ga^{3+}$ [6–8]. Among the metal dopants, Ga seems to be the best chemical element due to the fact that ionic radius of $Ga^{3+}$ (0.062 nm) is slightly smaller than $Zn^{2+}$ (0.074 nm) and the covalent bond length of Ga-O (1.92 Å) is similar to that of Zn-O (1.97 Å). Therefore, $Ga^{3+}$ can be substituted for $Zn^{2+}$ without much lattice distortion [9–11]. Joo et al. had successfully doped Ga into the ZnO nanorod arrays, and found that the photoluminescence spectra in the ultraviolet (UV) emission peak moves to long wavelength and the electrical properties of the Ga doped ZnO nanorod (GZO NRs)/*p*-Si diodes improved. They attributed it to the incorporation of Ga ionic enhancing the carrier concentration and reducing the defects of ZnO nanorods [12]. Jing et al. also had studied using hydrothermal method synthesizing the Ga doped ZnO nanobelts, and obtained the resistivity as low as $2.3\times10^{4}\ \Omega/cm^{2}$ [13]. However, the research on this aspect is not enough systemic, especially in the research of photodetector is still relatively small, which needs to make further exploration.

Owning to the high response speed and low noise absorption of Schottky type photodetector, it is more attractive. For the contact between the metal and n-type ZnO, many metals had been reported, such as Ta, Al, Ir, Ti, In, Pt, Pd, and Au [14–18]. Among these metals, Au is chosen widely for Schottky contact due to its high work functions, also its simple preparation process is the other reason. But as previously reported, the surface trap, adsorption material, hydrogen ions and surface polarity will all affect the ZnO surface and interface properties, so forming the stable and reliable Au/ZnO rectifying metal semiconductor contact is still a big challenge [15,19–23]. Therefore, it is necessary for the surface treatment of ZnO. A method of using sulfide surface treatment was reported to obtain ZnO/Pt Schottky contact by Seong et al. [24]. Also Seong found that hydrogen peroxide treatment can obtain ZnO/Pt Schottky contact [25]. In this paper, we reported a Au/GZO NRs/Au metal semiconductor metal (MSM) structure and in which GZO NRs were treated by hydrogen peroxide. We found through hydrogen peroxide treatment ohmic contact device was changed to a Schottky contact device, which showed a smaller dark current and faster response speed compared with ohmic contact device.

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http://dx.doi.org/10.1016/j.mssp.2017.03.023
Received 29 November 2016; Received in revised form 21 March 2017; Accepted 21 March 2017

## 2. Experimental section

### 2.1. Synthesis of GZO NRs

The doped and un-doped ZnO NRs used in this study were synthesized by a low temperature hydrothermal process, where different nominal concentrations (3%, 5% and 10%) of gallium were incorporated into the ZnO nanorods. ZnO nanorods were prepared by hydrothermal similar to the procedures in our previous study [26]. Firstly, the glass was cleaned in ultrasonic cleaners with deionized water, acetone and ethanol for 30 min, respectively, and then dried it by nitrogen before the UV cleaning treatment for removing organics. Then a ZnO seed layer was deposited onto the glass substrate by sol-gel technology. Secondly, a 90 nm thick ZnO seed layer was prepared by spin coating on FTO glass substrate with a speed of 5000 r/min, followed by being annealed at 350 ℃ for 2 h in air. As for the preparation of ZnO NRs array, the FTO glass deposited ZnO seed layer was immersed in an aqueous solution of 0.05 M zinc acetate (Zn $(CH_3COO)_2{\cdot}2H_2O$) and equivalent molar hexamethylene tetramine (HMT, $C_6H_{12}N_4$). In order to obtain the Ga doped ZnO NRs, nominal 0%, 3%, 5%, 10% gallium nitrate was put into above aqueous solution (normal Ga mol% = Ga[M]/Zn[M] × 100%). The samples were soaked in the aqueous solution with 8 h at the temperature of 90 ℃. Finally, the samples were rinsed with deionized water and dried in the air.

### 2.2. Hydrogen peroxide treatment

The prepared GZO NRs were immersed in a concentration of 30% hydrogen peroxide in 100 ℃ heated 3 min, and then GZO NRs were cleaned with deionized water and dried in air.

### 2.3. Electrode preparation

The Au electrode was prepared by an interdigital mask with a finger of 0.1 mm. Under a vacuum of $1\times10^{-3}$ Pa, the Au electrode was prepared by thermal evaporation with a thickness of 50 nm.

### 2.4. Measurement and analysis

The morphology and crystallinity of the samples were characterized by field emission scanning electron microscopy (FESEM,JEOL, JSM-6700F) and X-ray diffraction (XRD, D8 FOCUS X-ray diffraction), respectively. All the current-voltage (*I-V*) and current-time (*I-T*) characteristics were measured by a Keithley 4200 electrometer. The photosensitivity was studied using a 7LPD30 deuterium lamp source (30 W) with the wavelength from 200 to 400 nm. The actual optical power density was 30.5 W/m$^2$ in the location of our test. The sample was under direct illumination, and the optical power of light was measured by a UV-enhanced Si detector.

## 3. Results and discussion

The SEM images of surface morphology of GZO NRs with different Ga concentration are shown in Fig. 1(a)–(d). From the figures, GZO NRs grown by hydrothermal method are very orderly and good orientation with clean surface without residue, also the diameter of nanorods increases with the increase of Ga doping concentration. Thus, we believe that gallium ions have been doped into the crystal lattice rather

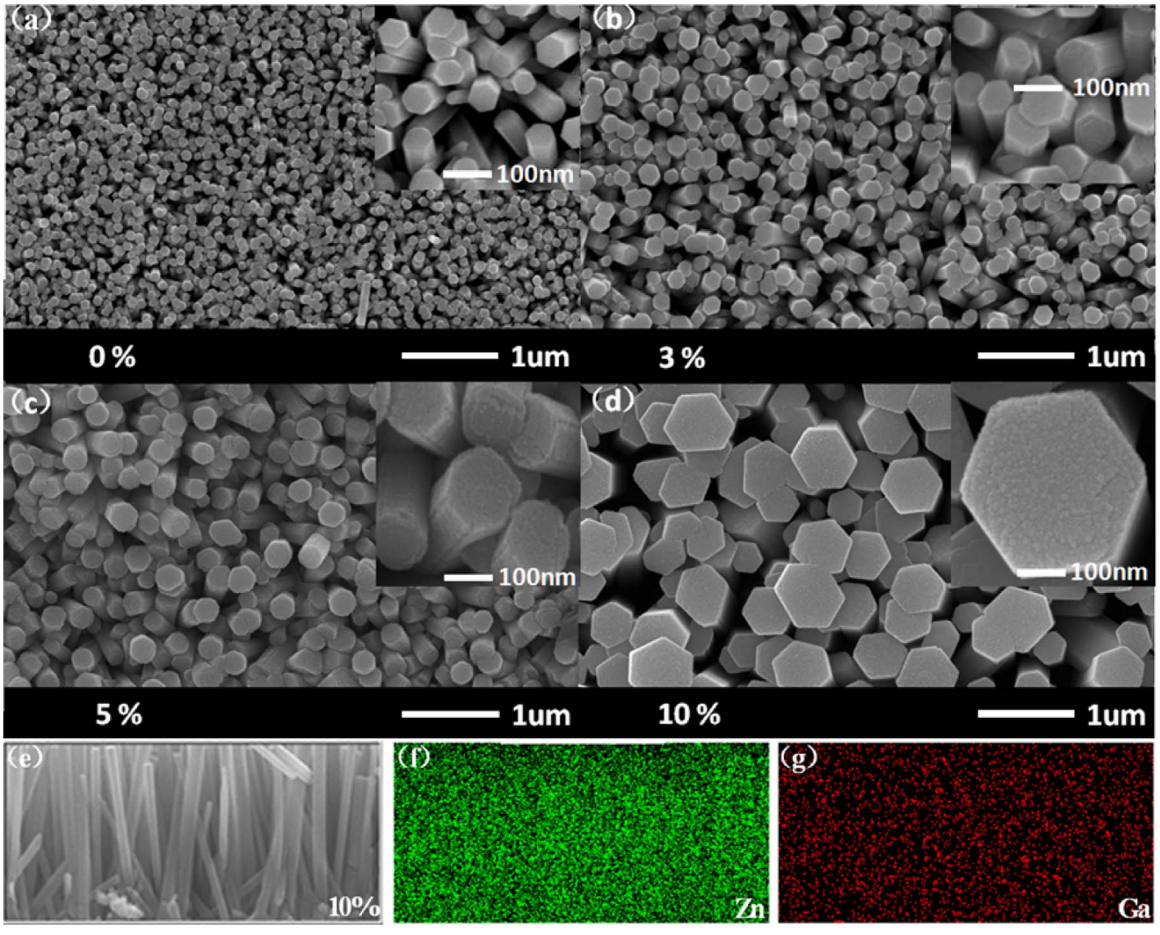


**Fig. 1.** Top-view SEM images of the GZO NRs with the Ga doping ratio of 0% (a), 3% (b), 5% (c) and 10% (d). (e) Cross-sectional view of SEM image of the 10% GZO NRs. The corresponding EDX mapping: Zinc distribution (f) and gallium distribution (g).