Physica E 57 (2014) 113–117

Contents lists available at ScienceDirect

Physica E

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

Optical and electrical properties of N-doped ZnO heterojunction photodiode

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HIGHLIGHTS

- High quality N-doped ZnO nanowires were grown on n-GaN substrates.
- Lasing characteristics are evident by using optical pumping.
- The *I–V* characteristics of the sample show a rectifying diode behavior.
- Distinct light emission in pumping current could be observed in the samples.
- The pure ZnO sample was synthesized for comparative studies.

ARTICLE INFO

Article history:
Received 13 August 2013
Received in revised form
29 October 2013
Accepted 31 October 2013
Available online 15 November 2013

Keywords:
ZnO nanowire
Heterojunction
Optical property
Electrical property

ABSTRACT

ZnO photodiodes consisting of high quality N-doped ZnO nanowires grown on n-GaN layer covered c-plane sapphire wafers were reported in this paper. The Au catalyzed ZnO nanowires were grown by chemical vapor deposition with excellent wurtzite structure. The *I–V* characteristics of the photodiodes show a rectifying diode behavior. Moreover, the pure ZnO/n-GaN sample was compared and analyzed to verify the p-type conductivity of heterojunction devices. We confirmed that such p-ZnO/n-GaN heterojunction devices exhibit distinct light emission when the electrode is applied with forward bias voltage. The lasing behavior of the p–n junction showed a threshold of 406 mW/cm^2 by using optical pumping. The realization of p-type ZnO nanowire arrays with durable and controlled transport properties is important for the fabrication of nanoscale electronic and optoelectronic devices.

1. Introduction

One-dimensional nanostructures have attracted much attention due to their potential applications in electronic and photonic devices [1–3]. ZnO has been widely used for applications in photonics, electronics, information storage, biology and medical therapeutics [4]. ZnO-based random lasing has been demonstrated with both optical and electrical pumping [5,6]. Although heterojunctions with ZnO nanostructures have been successfully developed with n-type ZnO on p-type substrates [7,8], only a few studies have been reported regarding the p-typed ZnO photodiodes [9]. The development of ZnO p–n junctions have been limited by the difficulty of growing p-type ZnO, since the realization of p-type ZnO is a still challenging due to its asymmetric doping limitations leading to the lacking of efficient ZnO-based laser devices [10].

ZnO nanowires can be grown by various techniques, such as vapor phase transport, hydrothermal synthesis, pulsed laser deposition (PLD), and chemical vapor deposition (CVD), etc. Using appropriate growth parameters, ZnO nanowires can grow spontaneously and their synthesis has been extensively reported. It is well-known that the physical and chemical properties depend on morphology, doping elements, doping concentrations, fabrication technologies, etc. Many research have been focused on the incorporation of N in ZnO nanowires [11,12], although Lyons et al. have predicted that N doping may not produce p-type ZnO [13]. Among the group-I and group-V elements, N has the shallowest acceptor level and smallest ionization energy, so N is the best elemental dopant source for p-type ZnO [14]. Recently, Hwang et al. grew a phosphorus doped p-ZnO layer on n-GaN substrates by magnetron sputtering [15]. Yuan et al. reported CVD growth of N-doped p-type ZnO nanowires by using N_2O as a doping source [16]. However, the optical and electrical properties of p-type ZnO nanowires p–n junction devices have rarely been studied.

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http://dx.doi.org/10.1016/j.physe.2013.10.038

In this work, the growth and properties of ZnO/GaN heterojunction devices are reported. High quality ZnO nanowires were grown on n-type GaN layer covered c-plane sapphire wafers by CVD in the atmosphere of N_2, for which Au droplets acted as a catalyst. Another ZnO nanowires were grown in Ar atmosphere for comparison, and all the other conditions are the same. These two different samples were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-Ray Diffraction (XRD), micro-Raman spectroscopy, photoluminescence (PL) and current–voltage (I–V) measurements. These results confirm the formation of p-ZnO/n GaN heterojunctions.

2. Experimental details

Commercial c-plane sapphire wafers with 2 μm thick c-plane oriented n-type GaN films were used as substrates. The vertically aligned ZnO nanowire arrays were synthesized on the GaN film by CVD process. The substrates were partially covered during the growing process of nanowires to expose the covered pure GaN films for the contact of the electrodes.

Before the growth of the ZnO nanowires, a 5 nm thick Au film was first deposited on the GaN surface as a catalyst by thermal evaporation. Mixture of ZnO and graphite powders with the same mass ratio was used as the source. All the chemicals are of AR grade. In order to control the release rate of the source, the powder was loaded in a small quartz tube of 6.5 mm diameter which was put in an alumina boat. Then the boat with source materials was positioned in the centre of the quartz tube. The substrates were kept 6 cm away from the source on the downstream side. For growing the N-doped ZnO nanowires, a flow of 1200 sccm (cubic centimetres per minute at STP) high purity N_2 passed continuously through the quartz tube. The quartz tube was then heated to 900 °C at a heating rate of 20 °C/min. Once the desired temperature was reached, 30 sccm O_2 was introduced into the quartz tube, with growing time maintained for 30 min. Meanwhile, the system pressure was maintained at 300 Pa. After the growth of the nanowires, the tube was naturally cooled down to room temperature. In order to confirm the effect of N doping on the p-type conduction, n-typed ZnO nanowires grown on n-typed GaN substrates (n-ZnO/GaN) in high purity Ar/O_2 atmosphere were synthesized under the same conditions for comparative studies.

After the vertical nanowire arrays were grown by CVD, the Au electrodes were deposited on the clean n-type GaN surface (partially covered during the nanowire growing process) for the Ohmic contact. The positive electrode was made through the following three steps. Firstly, PMMA (99.999%, Sigma Aldrich) crystal was dissolved in tetrahydrofuran to yield a solution with mass proportion of 5%. Then it was stirred for 2 h to prepare clear and homogeneous liquid and aged at room temperature for 24 h. Secondly, by controlling the concentration and spin rate, ultimately achieving an excellent effect where the solution completely filled the gap between ZnO nanowires and the top of nanowires was covered only by the thin layer. Typically the resultant solution was spun at an optimized rate of 3000 r.p.m. for 30 s onto the sample, and this process was repeated five times. Then the sample was annealed in air at a temperature of 100 °C for 2 h. Finally, top indium tin oxide (ITO, 99.99%) electrode was deposited on the nanowires by PLD. The energy of the laser beam and the laser pulse were controlled at 350 mJ and 2000 times, respectively. During deposition, oxygen gas was introduced into the chamber with a pressure of 1.3 Pa [17]. Fig. 1 shows a schematic diagram of the device.

The morphology of the synthesized ZnO nanowires was studied by SEM (FEI Inspect F50). The compositions of the samples were analyzed by XPS with Al Kα X-ray source (ThermoFisher SCIENTIFIC). The crystal structure of the samples was analyzed by XRD with Cu Kα radiation (Rigaku SmartLab 3). Raman measurements were carried out on a Horiba Jobin Yvon LabRAM HR 800 micro-Raman spectrometer with 785 nm excitation under air ambient condition. The optical pumping was tested by a Nd:YAG laser 355 nm. The electrical property was measured by a Keithley 2400 Sourcemeter and a 2182 A NanovoltMeter. All measurements were performed at room temperature.

3. Results and discussion

3.1. Surface characteristics

The side-view and top-view SEM images of the N-doped ZnO nanowires are shown in Fig. 2 and its inset, respectively. The c-axis of the ZnO nanowires perfectly matches the growing direction of the underlying film, resulting in good vertical alignment of nanowire arrays. The length and average diameter of the ZnO nanowires are 7 μm and 120 nm, respectively. Electronic structure of the elements of N-doped ZnO nanowires sample were analyzed using XPS. All the XPS spectra were referenced to the surface impurity C 1 s line (284.8 eV) binding energy. XPS spectra of Zn 2p and N 1 s are shown in Fig. 3(a) and (b) respectively, from which N elements have been identified. The binding energy of Zn $2p_{3/2}$ and $2p_{1/2}$ are found at 1021.2 eV and 1044.2 eV, respectively. The observed peak positions of Zn 2p and N 1 s are quite consistent with the previous reports on ZnO nanostrutures [18]. Furthermore, the N 1 s peaks located at 399.6 eV, are due to N_0–Zn bonds formation.

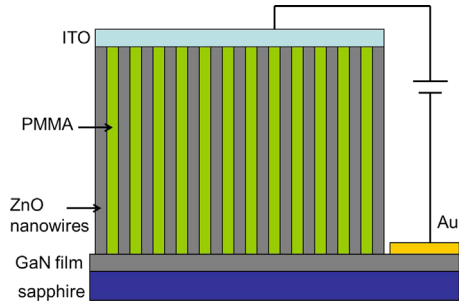

Fig. 1. Schematic of the heterojunction device, which consists of GaN thin film on sapphire substrates, N-doped vertically aligned ZnO nanowires, ITO contact and Au contact.

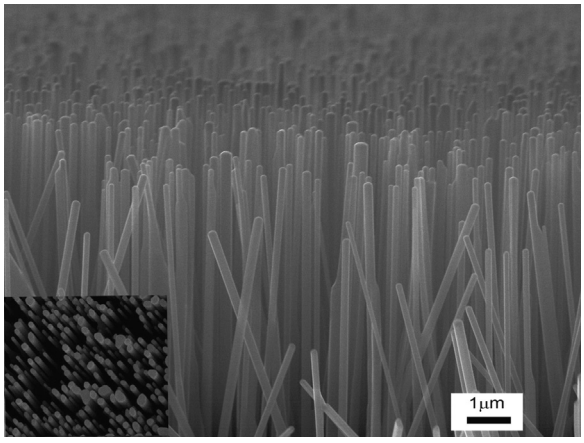

Fig. 2. Side-view and top-view SEM images of N-doped ZnO nanowires.