Fabrication and Characterization of Ultra Violet Photosensor based on Single ZnO Nanorod

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ABSTRACT

This article presents the fabrication and characterization of ultra violet (UV) photosensor, which utilizes the semiconducting properties of single ZnO nanorod. We report a study on the ZnO nanorods synthesized by an aqueous solution route in a hydrothermal reactor. Samples were characterized by X-ray diffraction, scanning electron microscopy, optical and electrical studies.

Our cost-effective synthesis method for ZnO nano/microrods permits easy transfer of sample and allows the study of fabrication of novel electronic nanodevices, such as gas and UV nanosensors. Our work is a starting point on the nanofabrication of optoelectronic nanodevices. It is anticipated to have a wide range of applications in space research, warning systems and accurate measurement of UV radiation.

Keywords: ZnO nanorod, nanosensor, UV, photosensor

1 INTRODUCTION

Wide-gap semiconducting metal oxides with nanostructures such as nanorods, nanowires are promising as building nanoblocks in novel nanodevices. These materials have been widely studied in the last few years due to their advantageous features such as good ultra-violet (UV) sensitivity to the ambient conditions [1]. Zinc oxide (ZnO) is an *n*-type metal oxide semiconductor with wide band gap of *E*g = 3.36 eV at 300 K. Zinc oxide can be used for UV detection owing to its characteristics and radiation hardness, high chemical stability, low cost and flexibility in fabrication [2-4]. These properties enable it to be used also in harsh environment [5].

Recently, ZnO nanorods and nanowires have been extensively investigated for sensors and optoelectronic device applications due to it's compatibility with other microelectronic devices. ZnO nanorods are expected to have good UV response due to their wide band-gap and large surface area to volume ratio, and they might enhance the performance of UV photosensors due to longer photocarrier lifetime and shorter charge carrier transit time.

It has been reported, *n*-type ZnO nanowires arrays/*p*-type Silicon UV photodetector [6], UV sensors based on nanostructured ZnO spheres in network of nanowires [1], multiple ZnO nanowires bridging the gap between the patterned Zn electrodes were studied as UV photodetector [7]. But, fabrication and characterization of a single ZnO nanorod-based photosensor can help in understanding the uniqueness of nanorods for photosensor and enable the design of novel devices. Thus, one-dimensional (1-D) nanorod attracted attention due to their unique properties that strongly depend on their size and morphologies and their possible use as building blocks in near-future UV nanodevices [1,6,7]. Our extensive effort and novel synthesis routes are currently devoted to the controlled synthesis and characterization of transferable ZnO nanoarchitectures. In this report, a new fabrication method of a UV photosensor based on single ZnO nanorod using in situ lift-out technique is presented for the first time. A new type of UV photosensor have been characterized and demonstrated that could detect UV light down to 50 nW cm^{-2} intensity, indicating a higher UV sensitivity than ZnO thin films.

2 EXPERIMENTAL

2.1 Synthesis

The ZnO nanorods in this study were synthesized via aqueous solution deposition technique, which has been previously reported in our work [8, 9]. This technique was found to have advantages of easy scaling and low cost.

All used reagents were of analytical grade and used without further purification. The glass substrates were cleaned according to procedure described in [8].

Zinc sulfate and sodium hydroxide solution were added into 75 ml DI–water under stirring to obtain a transparent solution. Then, the glass substrates and complex solution were transferred inside an aqueous solution in a reactor of 100 ml capacity and sealed. The setup was mounted on a hot plate, and the temperature was increased to 90 °C and kept constant for 15 min and then cooled down naturally to room temperature. Variation of the synthesis conditions such as concentration of precursors and temperature allow

certain degree of control on the growth rate and morphology of the obtained nanorods. Finally, the samples were rinsed in deionized water and dried at 150 °C, 5 min.

2.2 Characterization

The crystalline quality and orientations of ZnO nanorods were analyzed by an X-ray diffraction (XRD) using a Rigaku (Japan) 'D/B max' X-ray diffractometer equipped with a monochromatized CuKα radiation source (λ=1.54178 Å). The microstructure of the ZnO nanorods was observed by using scanning electron microscope (Hitachi S800). Transmission electron microscopy micrographs were carried in a FEI Tecnai F30 TEM at an accelerating voltage of 300 kV. The different characterization techniques confirmed that the nanorods are highly crystalline. Current-voltage (*I-V*) characteristics were measured using a semiconductor parameter analyzer with input impedance of 2.00×10^8 Ω. The UV sensing properties were characterized using a computer-controlled sensing characterization system.

3 NANOFABRICATION OF THE PHOTOSENSOR BY IN-SITU LIFT-OUT TECHNIQUE IN FIB INSTRUMENT

Next the procedure for UV photosensor fabrication is described. A micromanipulator was mounted beside the stage in FIB instrument. For the nanosensor preparation, the glass substrate was used and Al electrodes were deposited as template with external electrodes/connections. The needles used for the lift-out step were electro-polished tungsten wire. The ZnO nanorod has been transferred from initial glass substrate to the Si/SiO_2 substrate in order to avoid charging problems during of the pick-up step.

The next step in our procedure is to scan the surface of the intermediate Si/SiO_2 substrate for suitable ZnO nanorod. Then the W needle was lowered and bringing into the FIB focus and its tip positioned at one end of the ZnO nanorod. In the in-situ lift-out process [9], we found that attachment of single intermediate nanorod on the top of the FIB needle will permit an easy pick-up of the selected nanorod to be further handled. This step makes the fabrication of nanodevice much more efficient.

The needle was moved to one end of the nanorod (Fig. 3a). Then the nanorod was attached to the end of the FIB needle using Pt deposition of 0.5 μm thickness. In this step the nanorod attached to the end of the FIB needle is placed on the desired area with external connections for further sensor fabrication.

The nanorod is cutoff and the needle moves away from the substrate. In the Fig. 3b is shown ZnO nanorod fixed at both ends to the substrate with contacts.

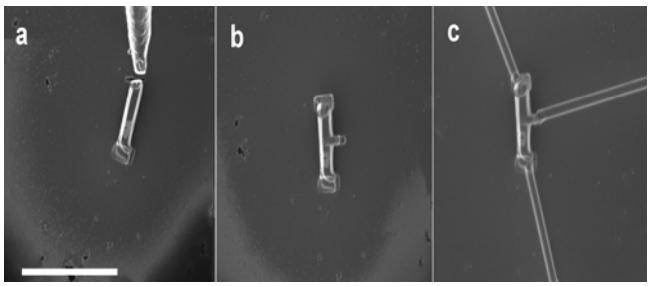

Figure 3: SEM images showing the steps of the in-situ lift-out fabrication procedure in the FIB system. (a) cutted from the W needle and placed the ZnO nanorod on substrate; (b) single nanorod fixed at both ends on substrate; (c) single nanorod welded to three electrode/external connections as final UV nanosensor. The scale bar is 5 μm.

In the last step, the nanorod was fixed to the pre-deposited electrodes/external contacts. Figure 3c show a novel single ZnO nanorod-based sensor fabricated by in-situ lift-out technique in the FIB system. By this technique, different shaped-nanosensors have been fabricated and investigated for their UV sensitivity.

The typical time taken to perform this in-situ lift-out FIB nanofabrication is about 25 min and our success rate is >95%. Also taken in the account that nanorod synthesis was done in 15 min, we substantially improve the fabrication process. This minimizes the time to fabricate nanodevices using FIB and can be extended to other specific nanodevices.

4 RESULTS AND DISCUSSIONS

Figure 1 shows the indexed XRD pattern of the ZnO nanorods in the range of 30-90° shows a predominant sharp peak at 36.2°, which is preferentially oriented (101) plane growth (Fig. 1). It can be seen that all diffraction peaks are caused by crystalline ZnO with the hexagonal wurtzite structure (space group: $P6_3mc$(186); the lattice constants a = 0.3249 nm, c = 0.5206 nm), which indicates that pure ZnO can be obtained at 90°C for 15 min. The data are in agreement with the JCPDS 036-1451 card for ZnO [10].

The morphology of the ZnO nanorods grown on glass substrate without using any templates was observed by the scanning electron microscopy (SEM). Typical SEM images of the ZnO nanorods are shown in Fig. 2. The SEM images of ZnO nanorods after annealed at 650 °C, 60 sec do not differ from those shown in Fig. 2.

In the inset image, it is clearly seen that ZnO nanorods with an average radius of 150 nm and are uniformly on its length. The medium lengths of ZnO nanorods are about 10 μm.

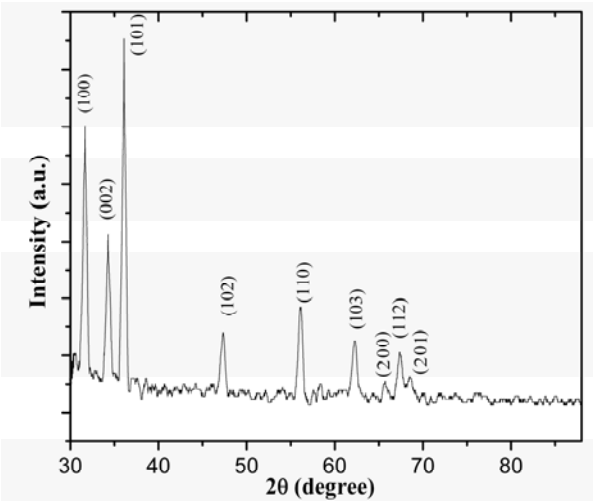

Figure 1: Indexed XRD scan for ZnO nanorods on glass substrate synthesized by the aqueous-solution method showing a wurtzite type structure.

According to our experimental results, the ZnO nanorods obtained by our process can be easily transferred to other substrates and handled by Focused Ion Beam (FIB) system in order to fabricate different nanodevices.

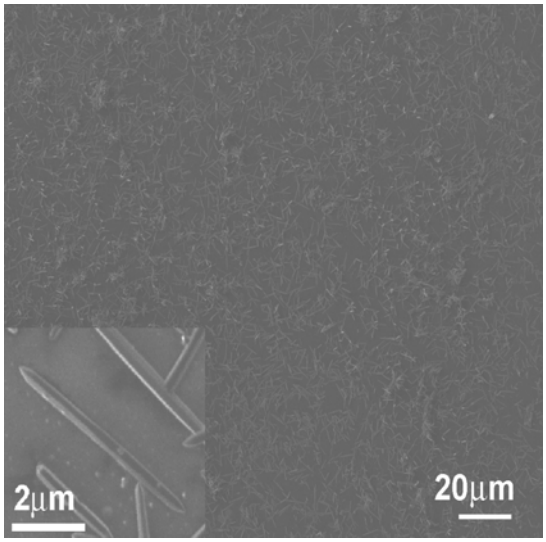

Figure 2: The SEM images of the ZnO nanorods on glass substrates and inset are individual rod image.

The detailed structural characterization of single ZnO nanorod was demonstrated by the high-resolution transmission electron microscopy (HRTEM) image [8].

5 UV SENSING

Next, we measured the *I*-V curves of the ZnO nanorod with connections realized by in-situ lift-out method. Figure 4 outlines the *I-V* characteristics of a three-terminal ZnO nanorod based photosensor in ambient air. The *I-V* measurements were performed by changing the bias voltages from +8 mV to -8 mV and vice versa. The voltage increment and delay time were set to 1 mV and 2 s.

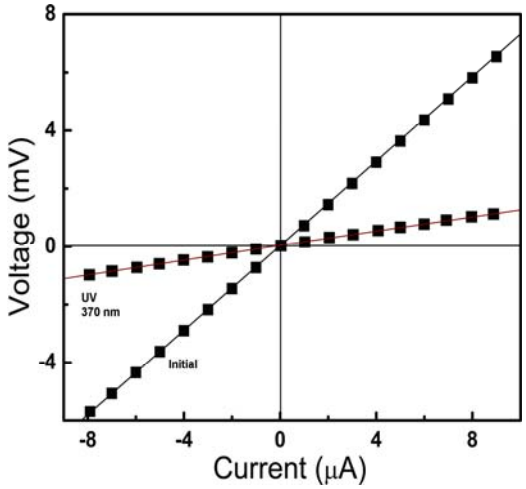

Figure 4: I-V characteristics of the ZnO – single nanorod photosensor without and under UV exposure at 370 nm.

The UV sensitivity was measured using ZnO nanorod device. The fabricated single ZnO nanorod-based sensor was put in a test chamber to detect ultraviolet light. The readings were taken after a UV light was turned on. It was subjected to irradiation with an UV light using a lamp with an incident peak wavelength of 370 nm with conductivity monitoring. The background atmosphere was air. It was found that conductivity change increased linearly with ultraviolet intensity. Due to the fact that the photon energy is higher than the bandgap of ZnO, UV light was absorbed by the ZnO nanorod creating electron-hole pairs, which were further separated by the electric field inside ZnO nanorod contributing to the increase of the conductivity.

When the ZnO nanorod photodetector was illuminated by 370 nm UV light, the conductance increased with a time constant of a few minutes as shown in Fig. 5. When the UV light was turned off, the conductance decreased back within 10% of the initial value (Fig. 5).

Response time constants are on the order of few minutes and after the signal reach the equilibrium value after the UV light was applied. This suggests a reasonable recovery time. The sensor showed relatively fast response and baseline recovery for UV detection.

Several photodetector on single nanorod have been fabricated by in-situ lift-out technique and investigated under identical conditions and was observed similar UV response. Spectral response demonstrates that such photodetector is indeed suitable for detecting UV in the range 300 nm – 400 nm.

The UV response is slow for ZnO nanorod photosensor and can be explained by the adsorption and photodesorption of ambient gas molecules such as O_2 or H_2O [3, 11]. The optical power on the detectors 50 nW so the photoresponsivity at 370 nm is 40 A/W.

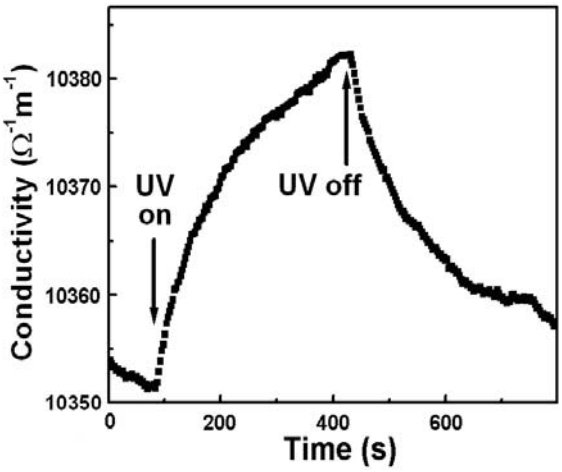

Figure 5: The conductivity response of the single ZnO nanorod-based UV photosensor fabricated by in-situ lift-out technique in the FIB system.

As-grown ZnO nanorod adsorbs oxygen molecules on the surface. Then will take free electrons from the *n*-type ZnO nanorod to form a depletion region. After UV illumination of photosensor the electron-hole pairs will be generated. The holes will recombine with oxygen ions chemisorbed on the surface and eliminate the depletion region [12]. At the same time the electrons produced will contribute to conductivity. Thus the time it takes electrons and holes to recombine will increase. Delay in the recombination of an electron and hole will increase, in this case the number of transit times for electron in the nanorod will be more than one. This phenomenon can lead to the increase in current and results in internal photoconductive gain.

The transit time of the charge carriers though the ZnO nanorod UV sensor can be described by [12]:

$$T_{tr} = \frac{d^2}{\mu_n V_b} \qquad (1)$$

where d - interelectrode spacing, μ_n - mobility of the electron, and V_b is the applied bias voltage. Thus, by using shorter interelectrode spacing d, the photoresponse speed can be improved. Also, by avoiding high temperatures processes during of the fabricating Al electrodes, by avoiding acid medium during the preparation of the sensor we can keep real bias voltage V_b and lower T_{tr} .

In addition, ZnO nanorod has high crystal and optical quality [8], so μ_n will be high. Thus we can shorten the transit time by decreasing recombination of charge carriers.

Thus UV light will hit the nanorod surface and will be generated electron-hole pairs. Electrons must remain free from holes long enough to zip along the nanorod and generate electric current under applied electric field and this will be the detection of light.

6 CONCLUSIONS

In summary, fabrication of single ZnO – nanorod UV photosensor by in-situ lift-out technique in the FIB system is demonstrated. Our technique can fabricate sensors on single nanowire in order to study light detection with single photon sensitivity.

The main advantage of the proposed synthesis is its simplicity and fast growth method. An in-situ lift-out technique has been presented to fabricate single ZnO nanorod –based photosensor. The typical time taken to perform this in-situ lift-out FIB nanofabrication is 25 min. Also taken in the account that nanorod synthesis takes about 15 min, we contribute to overcome some obstacles for nanorods/nanowires sensor production.

This technique has a great potential to be used to fabricate single ZnO nanorod-based photosensor which can help in understanding the uniqueness of nanorods for photosensor and enable the design of novel devices.

In summary, the prototype device provides a simple method for nanorods synthesis and demonstrated possibility of constructing nanoscale photodetectors for nano-optics applications.

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