Facile fabrication of UV photodetectors based on ZnO nanorod networks across trenched electrodes[*]

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Abstract: Using a low temperature hydrothermal synthesis method, ZnO nanorod networks have been directly grown across trenched Au microelectrodes arrays, which were modified with a layer of ZnO seeds. The characteristics of the current–voltage (*I–V*) and the photoresponse were obtained both in the dark and under ultraviolet illumination. The bridged nanorod network demonstrated a highly sensitive response to UV illumination in atmosphere at room temperature. It can be useful for nanoscale optoelectronic applications, serving as chemical sensors, biological sensors, and switching devices.

Key words: semiconductors; nanorods; photodetector; sensors
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1. Introduction

In recent years, research into the synthesis, characterization, and physical properties of one-dimensional (1-D) ZnO nanostructures (e.g., nanowires, nanobelts, and nanorods) has attracted much attention since nanoscale devices composed of the 1-D ZnO are promising for numerous applications, such as nanoscale lasers[1], light-emitting diodes[2], chemosensors[3], and UV photodetectors[4−7]. Early approaches for fabricating ZnO nanoscale nanodevices included dispersing the isolated ZnO nanowires directly, then randomly depositing it onto prefabricated electrodes[3−5], or locating the predispersed nanowires with the aid of various microscopes and then patterning the electrodes via e-beam lithography techniques to form metal contacts to both terminals of a single or multiple ZnO nanowires[8−10]. However, these processes were costly, tedious, and time-consuming; moreover, the electrical behavior of the nanowires in the devices was inherently influenced by the substrate, since the high contact resistance could not be avoided. Therefore, substantial efforts have been devoted to seeking an alternate strategy, which guarantees that nanowires can grow *in situ* on prefabricated nanoscale devices[11−13].

In this paper, bridged ZnO nanorod networks were directly synthesized across Au microelectrode arrays, which have been modified with a layer of ZnO seeds via a low temperature hydrothermal synthesis method[14−16]. The optical and photoconductive properties of as-prepared ZnO devices were also investigated. This work provides a easy fabrication method for nanoscale UV photodetectors at low cost, which can easily be scaled up to mass production.

2. Experimental details

2.1. Materials

All chemicals were analytical-grade reagents and were purchased from Shanghai Chemical Reagent Corp. Zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] and hexamethylenetetramine ($C_6H_{12}N_4$) were used as reactants without further purification. All solutions were prepared with Milli-Q water (18.2 MΩ/cm).

2.2. Preparation of ZnO nanorods across the trenched electrodes

The gold microelectrode arrays were fabricated by using a conventional photolithographic method with a finger width of 10 μm and a gap of 1.2 μm. The fingers were made by thermally evaporating 30 nm Ti and 100 nm Au on a layer of silicon dioxide (SiO_2), which was thermally grown on top of a silicon wafer. The formation route of high-quality ZnO nanorods reported here was based on oriented attachment of preformed quasi-spherical ZnO nanoparticles in the trenches of the electrodes. Kang *et al.*[17] recently developed a technique of selective area growth of ZnO nanorods on the surfaces of other semiconductors or glass. For the experimental conditions of a modifying ZnO seed layer, the reder is refered to Ref. [18]. The growth of ZnO nanorods was done at 90 °C by suspending the substrates, which had been modified with ZnO seeds, into a Teflon vessel, which was filled with a mixture of an aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 0.01 M) and hexamethylenetetramine ($C_6H_{12}N_4$, 0.01 M). The reaction time was 3–5 h. After the reaction, the substrates were
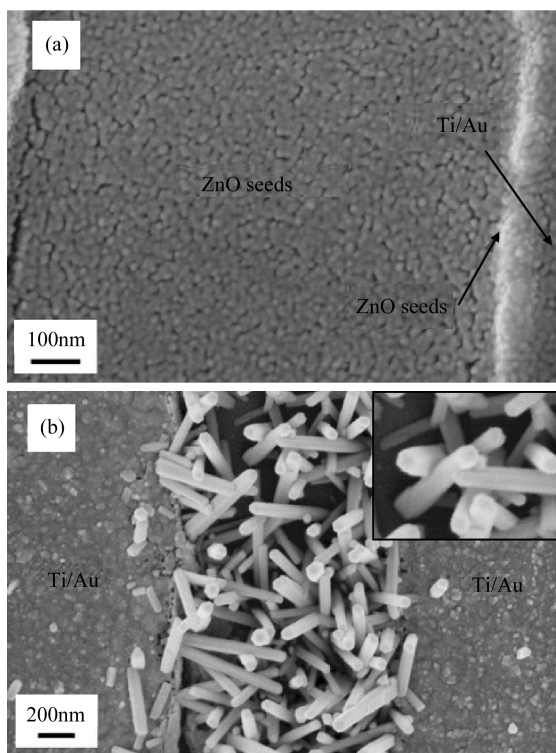

Fig. 1. (a) FE-SEM image of ZnO seed films used to modify the trench of the electrodes; (b) FE-SEM image of the ZnO nanorods grown between two electrodes.

Fig. 2. Room temperature PL spectrum of ZnO nanorods using an Xe lamp (λ_{ex}= 325 nm) for excitation.

removed from the solution, rinsed with deionized water, and dried. The nanorods on the top surface of the trenches can be removed by wiping the surface of the substrate. As a result, synthesized ZnO nanorods networks crossing the Au electrodes were formed between the two electrodes.

2.3. Characterization

The morphologies of the as-synthesized ZnO films and the interconnected ZnO nanorods were observed by using a field-emission scanning electron microscopy (FE-SEM, LEO1550). Photoluminescence measurements were carried out by using a CARYE Eclipse Fluorescence spectrum, which uses a Xe lamp as the excitation source. The characteristics of current–voltage (I–V) and the photoresponses of the ZnO nanobridge device were measured by an electrochemical instrument (CHI630B) under UV illumination at $\lambda = 365$ nm（hand-held UV-lamp, 0.3 mW/cm^2）.

3. Results and discussion

Figure 1(a) shows an FE-SEM image of the as-synthesized ZnO seed films on the trench of the electrodes. The seed surface is smooth and closely packed by the ZnO crystallites, and the average diameter of nanograins is ~15 nm. Figure 1(b) is an FE-SEM image of the synthesized ZnO nanorods between the gaps of the microelectrodes. These nanorods have a typically hexagonal shape and their diameters are about 50 nm. The orientation of the ZnO seeds directly determined the orientation of the nanorods[19]. The nanorods
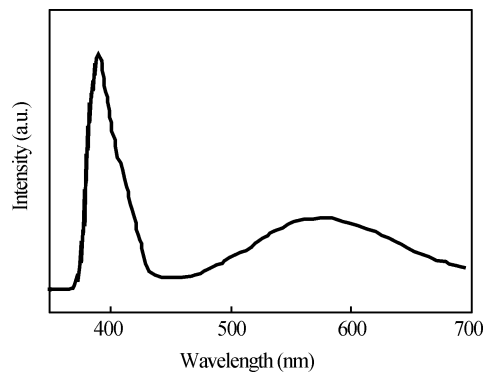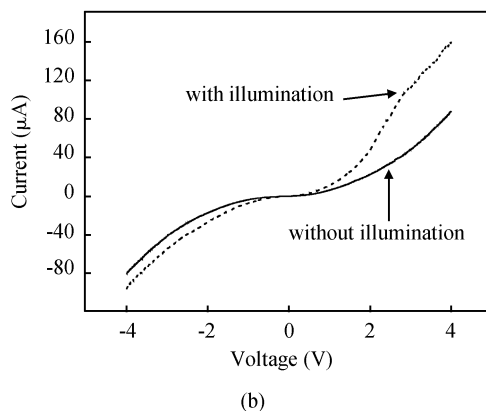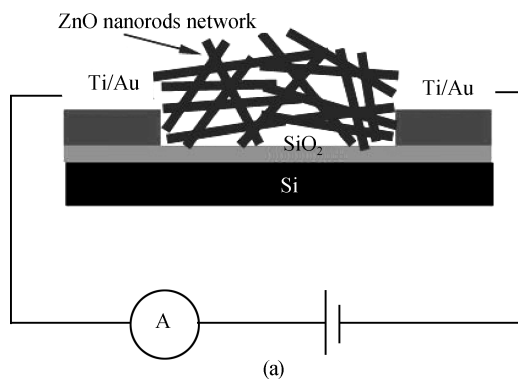

Fig. 3. (a) Schematic of the ZnO nanorod network photoconductor; (b) I–V characteristics of the ZnO nanorod network with and without UV (365 nm) illumination.

with different orientation intersected with each other and formed a network of nanorod bridges across the microtrench (Fig. 1(b)).

Room temperature photoluminescence (PL) nolinebreak measurement of the as-grown ZnO nanorods was carried out by using a Xe lamp (325 nm wavelength) as the source of excitation. Figure 2 shows the typical PL spectrum of the ZnO nanorods with a strong luminescence peak centered around 390 nm, which represents the near-band-edge (3.18 eV) emission, and a weak broad band centered around 570 nm, which could be attributed to deep-level defects in the ZnO crystals[20−22].

Figure 3(a) depicts a schematic diagram of the ZnO nanorod network UV photodetector. The two Au electrodes work in a two probe electrical configuration and the ZnO
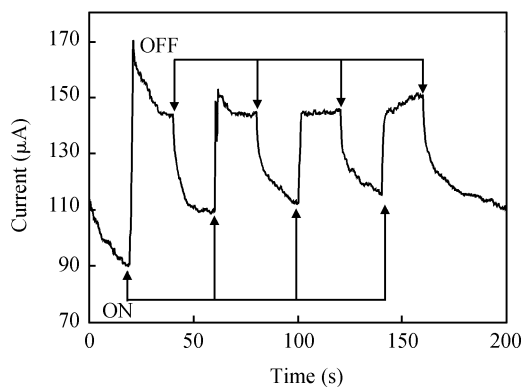
Fig. 4. Reversible switching of the ZnO nanorod network between low and high conductivity states when the 365 nm UV light was turned on and off, and the bias on the nanorods was 5.0 V.

nanorods, which bridge the electrodes, act as the conductive channel. Typical *I–V* characteristics of the synthesized networked ZnO nanorods in the dark and under UV ($\lambda = 365$ nm) illumination are shown in Fig. 3(b). The non-linear nature of the *I–V* characteristic measured in air at room temperature is likely due to the Schottky barrier formed between the electrodes and the ZnO nanobridges[11]. Due to some impurities segregated at the nanorod grain boundaries, originating from the impurities in the $Zn(NO_3)_2 \cdot 6H_2O$ (99%) precursor, it is still likely that electrostatic potential barriers across the multi-grain boundaries, which resulted in the varistor-like nonlinear *I–V* characteristics, are formed. The same results can be found in other reports[23−26]. It is well known that ZnO nanorods are highly sensitive to UV illumination, which creates a photocurrent. Indeed, the measured current of the nanorods "network nanobridges" was increased from 88.16 to 159.80 μA under UV illumination at an applied voltage of 4.0 V, as shown in Fig. 3(b). The highest photoresponsivity is about 1.22 A/W at 5 V bias under UV illumination.

Figure 4 presents the photoresponse of the networked nanorods in air for repetitive switching of the UV light ($\lambda = 365$ nm, 0.3 mW/cm^2) at a bias voltage of 5.0 V applied across the two electrodes. The characteristics of the photoconductive ZnO nanorods suggest that they are good candidates for optoelectronic switches, with the dark insulating state as "OFF" and the UV-exposed conducting state as "ON". It was evident that the nanorods could be reversibly switched between the low and high conductivity states. It was found that the photocurrent increased rapidly to more than 80% within 2 s. Afterwards it decreased rapidly and was followed by a relatively slow process.

Besides the photoexcited electron–hole pair mechanism ($h\nu \rightarrow e^- + h^+$), it is well known that the adsorption/desorption of oxygen on the surface is crucial to the increase/decrease of the conductivity for ZnO nanowire[4]. A similar mechanism was proposed to explain this networked "nanorod bridges" photoconduction behavior. In the dark, oxygen is adsorbed on the nanorod surface and negatively charged by capturing a free electron from the ZnO, thus, leaving a depletion region

near the surface. The negative oxygen ions adhered to the surface of the nanorods. They were not free carriers and could not contribute to the conductivity of the nanorods. Also, the oxygen adsorption introduced a potential barrier, which was unfavorable for the carrier mobility. Upon exposure to UV-light, photogenerated holes were captured by the negatively charged oxygen ions by surface electron–hole recombination. At the same time, the increase of the photogenerated electrons caused an accumulation of conduction electrons. In addition, the oxygen photodesorption also lowered the barriers height of the grain-boundaries and increased the mobility of the carriers[27]. As a result, the conductivity increased. The synthesized ZnO nanorods were connected between the electrodes to form a three-dimension interconnected network, and they contributed to the excited electron transport, resulting in the photoconduction. In general, the process of the adsorption of oxygen was longer than the process of desorption[7]. So, the time that it took for the current to decrease was longer than the rise time of the photocurrent when the UV-light was turned off.

4. Conclusions

In conclusion, large scale networked ZnO nanorods have been grown directly across trenched Au microelectrode arrays, which had been modified with a layer of ZnO seeds by using a low temperature hydrothermal synthesis. The interconnected network contributed to the excited electron transport, resulting in photoconduction. The results open up the possibility of mass production of simple, low-cost, and highly photosensitive UV photodetectors based on ZnO nanorods. These photoconducting networked nanorods could be useful for nanoscale optoelectronic applications serving as chemical sensors, biological sensors, and switching devices.

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