Original Research

High sensitivity, fast speed and self-powered ultraviolet photodetectors based on ZnO micro/nanowire networks

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Abstract

Ultraviolet (UV) photodetectors (PDs) based on ZnO micro/nanowire (MNW) networks with Pt contacts have been fabricated on glass substrates. The PDs exhibited a high photosensitivity ($5 \times 10^3$) for 365 nm UV light with a fast recovery time (0.2 s) at a reverse bias voltage of 2 V. The light induced modulation of Schottky barrier and MNW–MNW junction barrier was employed to account for the results. It was also observed that the PD had a high on–off ratio of 800 without external bias. The photovoltaic effect was proposed to explain the self-powered phenomenon.

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Keywords: ZnO; Photodetector; Network; Sensitivity; Response time

1. Introduction

With a direct wide-gap of 3.37 eV and a large exciton binding energy of 60 meV, ZnO has attracted considerable attention for the potential applications in optoelectronic devices [1–3]. ZnO nanowires possess large surface-to-volume ratio and good crystallinity [4], thus attracting an increasing amount of interest in the application of UV photodetection [5,6]. However, photoconductive PDs based on the ZnO NWs have a long recovery time in second scale due to oxygen-related hole-trap states at the NW surface [7,8]. Many efforts have been made to enhance the response speed of PDs based on ZnO NWs. For example, the reset time has been reduced from 417 s to 0.8 s by using Schottky contact instead of Ohmic contact in device fabrication [9]. It has been reported that the surface coating of polymer can reduce the UV response time of ZnO NWs [10]. Recently, C.Y. Yan et al. reported that PDs based on Zn$_2$GeO$_4$ NW networks had enhanced response speed, due to NW–NW barrier dominated conductance [11]. Nowadays the world is on the brink of energy crisis and low-energy or even zero-energy photoelectronic devices are extremely necessary. As a consequence, there has been a surge of interest in self-powered nanosensors, especially self-powered PDs [12,13], which could operate at zero bias without external power source.

In this letter, we demonstrated a self-powered UV PD based on ZnO MNW networks. Owing to the Pt/ZnO MNWs Schottky contact barrier and the MNW–MNW contact barrier, high photo-to-dark current ratio and rapid response speed were achieved. Furthermore, under zero bias, the fabricated device also showed a fast recovery time and a high sensitivity to UV light illumination.

2. Methods

The ZnO MNWs were synthesized via a non-catalyzed vapor deposition method. Mixed ZnO and carbon powder (molar ratio 1:1) as source materials were loaded onto a ceramic boat placed...
at the center of the tube furnace and heated at 900 °C for 15 min. The flow rates of Ar and O2 in the quartz tube were kept at 300 SCCM (cubic centimeter per minute at STP) and 3 SCCM, respectively. The ZnO MNWs were collected on the Si (100) substrates. Morphologies and structures of the products were characterized using scanning electron microscopy (SEM, JSM-6490) and X-ray diffraction (XRD, Rigaku DMAX-RB, Japan). The photoluminescence (PL) spectrum excited by a 325 nm He–Cd laser was recorded by a Raman spectroscope meter (Jobin-Yvon, HR800) at room temperature. For device fabrication, a 150 nm thick Pt film with a hole (5 mm in diameter) in the middle was first deposited on the glass substrate using DC sputtering to serve as an electrode. The ZnO MNWs were suspended in ethanol by sonication and then transferred to the gap of the Pt electrode. The high-purity silver conducting paint was placed on the ZnO MNW network to serve as Ohmic contact. The electrical transport property of the device was measured using a semiconductor characterization system (Keithley 4200-SCS). To characterize the photoresponse properties of the PD, a portable UV lamp (365 nm, 1 mW/cm²) was used as the light source.

3. Results and discussions

Fig. 1(a) shows the SEM image of ZnO MNWs grown on the Si substrate. The diameters of the MNWs range from 1 μm to 6 μm and the average lengths about tens of micrometers. It can be seen from the inset that the ZnO MNWs have well-resolved edges and smooth surface morphology. Fig. 2(b) depicts the XRD pattern of the as-grown ZnO MNWs. The peaks centered at 31.6°, 34.3°, 36.1°, 47.3°, 56.3° and 62.7° correspond to the diffraction planes (100), (002), (101), (102), (110) and (103) in ZnO with the hexagonal wurtzite, respectively. The high intensity (002) diffraction peak indicates that the MNWs are highly oriented and crystalline. The PL spectrum of ZnO MNWs excited by a 325 nm He–Cd laser is shown in Fig. 1(c). The sharp UV emission peak at 378.5 nm corresponding to the near band-edge emission is normally the result of the recombination of exciton [14]. In addition, a broad weak green emission is observed, which is related to the oxygen vacancies and some structural defects [15]. It should be noticed that the ZnO MNWs possess good crystallization since the green emission is almost negligible.

Fig. 2(a) shows the schematic diagram of the fabricated PD based on ZnO MNW networks. The I–V curve shows rectification characteristic, which makes it clear that good Schottky contact has formed between the ZnO MNW networks and the Pt film, because the work function of the Pt film is 5.6 eV higher than that of ZnO and the built-in potential barrier in ZnO MNW/Ag is quite negligible. The turn-on voltage is estimated to be about 1.5 V and the rectification ratio at ± 5 is about 70. According to the thermionic emission model, the typical I–V characteristic of the Schottky diode at forward bias,
for $V - IR_s > 3kT/q$, can be described as [16]

$$I = I_s \exp \left[ -\frac{q}{nkT} (V - IR_s) \right]$$

(1)

in which

$$I_s = A^{**}T^2 \exp \left[ -\frac{q\phi_b}{kT} \right]$$

(2)

where $I_s$, $n$, $k$, $R_s$, $A^{**}$ and $\phi_b$ are reverse bias saturation current, ideal factor, Boltzmann’s constant, series resistance, effective Richardson coefficient and barrier height, respectively, and the theoretical value of $A^{**}$ for ZnO is 32 A cm$^{-2}$ K$^{-2}$. From the $I$–$V$ curve measured at room temperature, the values of $n$ and $\phi_b$ were extracted to be 16 and 1.1 eV, respectively. Compared to the self-powered PDs based on ZnO NW arrays that have a large dark current in microampere range, our network PD has a dark current at the $10^{-10}$ A scale, because the conductance of the device is dominated by Schottky barrier and MNW–MNW junction barrier [11].

To display the photoelectric features of the fabricated PD, the $I$–$V$ characteristic was measured upon 365-nm UV illumination with a power of 1 mW/cm$^2$. From the $I$–$V$ curve, the nonlinear curve becomes almost linear on UV illumination, as a consequence of the increase in the carrier density in the ZnO MNWs and the reduction in the Pt/ZnO MNWs Schottky barrier[17] and the MNW–MNW junction barrier.

The photoresponse of the PD was characterized by measuring the current as a function of time when the 365 nm UV light was periodically turned on and off, as shown in Fig. 2(c). At a reverse bias of 2 V, the current rose from 0.002 nA to 10.4 nA, when UV was on. The sensitivity (photocurrent-to-dark current ratio) is about 5000 for the device. The rise and recovery processes of the photocurrent follow a biexponential relaxation equation [18]

$$I = I_0 + C_1 \exp \left( -\frac{t}{\tau_1} \right) + C_2 \exp \left( -\frac{t}{\tau_2} \right)$$

(3)

where $\tau_1$ and $\tau_2$ are time constants. The first time constant corresponds to the rapid recombination of photoinduced electrons in conduction band with photoinduced holes in valence band. And the second one is related to the slow process of desorption and adsorption of oxygen on the surfaces of ZnO MNWs. When ZnO MNWs were exposed to UV photons with higher energy than the bandgap of ZnO, oxygen ions adsorbed on their surfaces were neutralized by the photoexcited holes through $O_2^{-}\ (ad) + h^+ \rightarrow O_2(g)$, thereby releasing the electrons back to conduction band and thinning the shell depletion layer. When UV light was off, oxygen molecules were re-adsorbed onto their surfaces by capturing the photoexcited electrons through $O_2(g) + e^- \rightarrow O_2^{-}\ (ad)$, creating a shell depletion layer and reducing the carrier density in ZnO MNWs [7]. By fitting Eq. (3), the values of $\tau_1$ and $\tau_2$ for rise process are 0.29 s (0.2 s, corresponding time constant for recovery process) and 5 s (2.24 s) respectively. Compared to other nanowire/belt network PDs (see Table 1), our ZnO MNWs PDs exhibit relatively fast response time and enhanced...
UV sensitivity, which is attributed to two additional conducting mechanisms. The first one is related to the Schottky contact at the Pt/ZnO MNWs interfaces. When the 365 nm illumination was on, the photogenerated electron–hole pairs in the reverse-biased Schottky interface region were separated by the built-in electric field, resulting in an increase in free carrier density. When UV light was off, a handful of oxygen was readsorbed onto the interface of Pt/ZnO MNWs, resulting in a faster recovery time.

The other is related to the ZnO MNW–MNW junction barrier, which is derived from the shell depletion layer. Upon UV illumination, the MNW–MNW barrier height is lowered due to the thinning of the shell depletion layer of ZnO MNWs (see Fig. 3(b)). Therefore, it is easier for electrons to go through the networks under UV illumination, resulting in the increase of current. When UV light was off, the photoexcited electrons and holes would be quickly recombined and driven by the internal electric field near the interfaces of ZnO MNWs, resulting in a faster recovery time.

The rise time (the time taken by the PD to reach 63% of the maximum photocurrent from its dark current value) and the recovery time (the time taken to reach 37% times of the maximum photoresponse current) are 208 ms and 198 ms, respectively. To understand the self-powered phenomena, photovoltaic effect in the device was investigated. Upon 365 nm UV illumination, electrons and holes are generated in the ZnO MNWs. For the photocondutive PDs, no photocurrent can be observed because of the high recombination rate. In our case, the photoinduced carriers were swept away from the space charge region at the interface of Pt/ZnO MNWs driven by the strong built-in electric field (see Fig. 3(b)). The fast response time is due to the rapid separation and recombination of the photogenerated electrons and holes, which is related to the diffusion of carriers outside the depletion area and the drift of carriers inside the space charge region [23].

### 4. Conclusions

In conclusion, Schottky junctions between ZnO MNW networks and Pt film were fabricated for the application in self-powered UV PDs. High on–off ratio and fast decay time were achieved due to the resistance dominated by the Schottky barrier and MNW–MNW contact barrier. In addition, the PD has excellent photoresponse properties to 365 nm UV irradiation at zero bias. The results demonstrate that the PD based on the ZnO MNW networks is a promising candidate for fast speed and self-sufficient photodetection.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Device type</th>
<th>Light of detection (nm)</th>
<th>Intensity of light (mW/cm²)</th>
<th>Applied bias (V)</th>
<th>Sensitivity</th>
<th>Rise time (ms)</th>
<th>Recovery time (ms)</th>
<th>Reference</th>
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<td>Zn₂GeO₄ NW</td>
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<td>0.2</td>
<td>20</td>
<td>10</td>
<td>300</td>
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<td>990</td>
<td>1000</td>
<td>1000</td>
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<td>/</td>
<td>5</td>
<td>35</td>
<td>&gt; 4000</td>
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<tr>
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<td>2</td>
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<td>[21]</td>
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<td>640</td>
<td>1</td>
<td>300</td>
<td>/</td>
<td>530</td>
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<tr>
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<td>1</td>
<td>−2</td>
<td>5000</td>
<td>290</td>
<td>200</td>
<td>Our work</td>
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Fig. 3. (a) The photocurrent response curve of the PD under UV illumination being turned on and off at zero bias. (b) Schematic of the carrier generation, Schottky barrier and MNW–MNW junction barrier for electron transfer in the ZnO MNW network PDs.
Acknowledgments

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