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Research Article

Enhanced Response Speed of ZnO Nanowire Photodetector by Coating with Photoresist

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Spin-coating photoresist film on ZnO nanowire (NW) was introduced into the fabrication procedure to improve photoresponse and recovery speed of a ZnO NW ultraviolet photoelectric detector. A ZnO NW was first assembled on prefabricated electrodes by dielectrophoresis. Then, photoresist was spin-coated on the nanowire. Finally, a metal layer was electrodeposited on the nanowire-electrode contacts. The response properties and *I-V* characteristics of ZnO NW photodetector were investigated by measuring the electrical current under different conditions. Measurement results demonstrated that the detector has an enhanced photoresponse and recovery speed after coating the nanowire with photoresist. The photoresponse and recovery characteristics of detectors with and without spin-coating were compared to demonstrate the effects of photoresist and the enhancement of response and recovery speed of the photodetector is ascribed to the reduced surface absorbed oxygen molecules and binding effect on the residual oxygen molecules after photoresist spin-coating. The results demonstrated that surface coating may be an effective and simple way to improve the response speed of the photoelectric device.

1. Introduction

ZnO is a semiconductor material with a direct energy band gap of 3.37 eV and a large excitation binding energy of 60 meV at room temperature. Different fields have studied the potential applications of ZnO, such as transistors, photodetectors, piezoelectric devices, solar cells, and sensors [1–6]. Recently, ZnO semiconductor nanowires, nanobelts, and nanoparticles with characteristic of high surface-to-volume ratios have emerged as remarkable nanomaterials in various fields. For example, Soci et al. [7] demonstrated that the optical internal gain of ZnO nanowire (NW) ultraviolet (UV) photodetectors could reach as high as ~10^8, and this gain shows their potential application in gain-bandwidth products. However, two fundamental limitations remain to be overcome in the application of ZnO NW UV photodetectors. First, surface absorbed molecules [8–12] or surface defects [13] can deteriorate the performance of a ZnO NW device; in particular, the absorption and desorption of the oxygen molecules from the surface of ZnO NWs can affect the performance of the devices. Second, surface contamination [14, 15] produced during the synthesis process and the assembly process may result in poor metal-semiconductor contacts and even nonsymmetrical contacts; these poor contacts lead to the poor performance of ZnO NW devices.

Surface functionalization has been proved to be an effective way to modify surface physical properties of ZnO NWs. Indeed, it can be used to enhance the electrical and optoelectronic performance of ZnO NW devices [16]. However, the functionalization processes [17] for the fabrication of ZnO

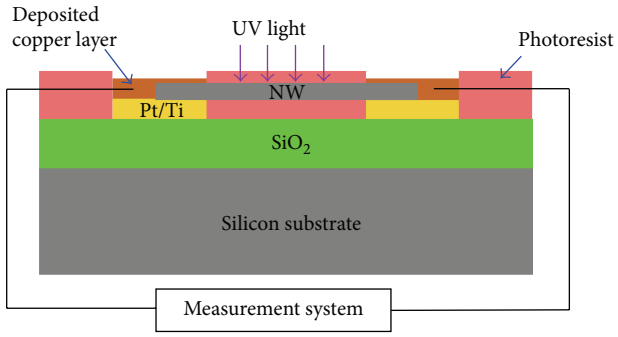

Figure 1: ZnO NW UV photodetector structure with photoresist and electrodeposited copper.

NW device are mostly complex. As to surface contamination, annealing at high temperatures and focus ion beam- (FIB-) assisted deposition [10] are two commonly used methods to improve the metal-semiconductor contacts. However, the high temperature used in annealing may cause unpredictable damage to the devices, and FIB-based metal deposition is inefficient and costly.

In this paper, we report an approach implemented by the functionalization of a ZnO NW with photoresist to enhance the response characteristics of a ZnO NW UV photodetector. Positive photoresist AZ 1505 is a mixture of polymers and other compounds. It is a type of material used for photolithography that has a transparent appearance and good adherence. To further improve the performance of the device, a much cheaper and simpler fabrication method of electrodeposition [18] is implemented to deposit metal on electrodes. In the present work, the photoresist was adopted as the coating material of ZnO NWs, and a photolithographed photoresist pattern was used as the mold of metal deposition.

2. Principle and Methods

The structural diagram of a ZnO NW-based photoelectric photodetector is illustrated in Figure 1. Pt electrodes were fabricated on a silicon substrate and were isolated by an 800 nm SiO_2 layer. ZnO NW was assembled on the Pt electrodes to form the channel of carriers, which could detect UV photons. The photoresist coating is isolated O_2 from the ambient atmosphere. Thus, the absorption and desorption processes of O_2 were prevented and thus the response and recovery speed of the photodetector were enhanced. Two electrodes were electrodeposited by the metal layer to form good metal-semiconductor contact with the help of the photoresist pattern. At the same time, the deposited copper used in this work had a lower work function than the Pt electrodes, and the deposited copper layer could enlarge the contact area of the metal-semiconductor contacts, thus forming ohmic-type metal-semiconductor contacts.

3. Experimental Details

3.1. Fabrication of Electrodes and Assembly of ZnO NWs. ZnO NWs were synthesized on an alumina plate by a catalyst-free solid vapor process under controlled conditions [19]. ZnO NWs were suspended in an ethanol solution by sonication. Figure 2 briefly illustrates the fabrication procedures of the basic photodetector. The parallel electrode patterns were defined by a standard photolithography procedure.

In general, dielectrophoresis [20–22] is a simple, effective, and controllable method to assemble ZnO NW devices. Thus, ZnO NWs were assembled onto the electrodes through dielectrophoresis (Figure 2(d)) in the present work. After applying an AC voltage ($V_{p\text{-}p}$ = 5 V, f = 1 MHz) across the electrodes, a 5 μL droplet of ZnO NW suspension was dropped onto the electrodes; the AC power source was cut off after a few minutes. The chip was rinsed with ethanol for 10 s and then with deionized (DI) water for 15 s. Then, it was dried using a gentle stream of nitrogen gas for 15 s. A thermal annealing process was conducted in a vacuum annealing box at 300°C for 3 h to improve the contacts of the nanowires and electrodes and to remove the residual ethanol from the nanowire surface.

3.2. ZnO NW Surface Functionalization and Electrodes Electrodeposition. First, we stabilized the nanowires on the substrate using an electrical adsorption process, that is, by applying a pulsed voltage (V_p = 5 V, f = 1000 Hz) across the electrodes for a few minutes. Second, photoresist was spin-coated on the chip (Figures 3(a) and 3(b)). After conducting aligned lithography (Figures 3(c) and 3(d)), the electrodes were exposed and the ZnO NWs were immobilized in the photoresist. Lastly, we electroplated a copper layer on the Pt electrodes by dropping a cupric nitrite electrolyte solution onto the electrodes (Figure 3(e)) and by applying a DC bias of 5 V for 5 min (Cu $(NO_3)_2$ 400 g/L, Cl^- 50 ppm, PEG6000 10 ppm, and current density 1 A/dm^2) [18]. After electrodeposition was performed, the chip was rinsed with DI water and dried with a gentle stream of nitrogen gas.

Time-related photocurrent was recorded at a constant DC bias of 5 V as the illumination of UV light (λ = 365 nm, approximately 30 μW/cm^2) was turned on and off. The current-voltage curves were recorded under dark conditions by Keithley 6487 picoammeter.

4. Results and Discussion

4.1. I-V Characteristics of the Nanowire Photodetector. Figure 4 compares the typical *I-V* characteristics of the nanowire photodetector without photoresist coating before (red curve) and after (black curve) electrodeposition. *I-V* characteristics were measured at room temperature by the picoammeter under dark conditions. The black curve shows a noticeable decrease in resistance compared with the red curve; this decrease demonstrates that a good ohmic-type device was fabricated after electrodeposition. This decrease may be due to the fact that the work function of copper (4.51 eV) is closer to the electron affinity of ZnO (4.1 eV) than the work function of platinum (5.64 eV). At the same time, the deposited copper covering on the Pt electrodes and nanowire can enlarge the contact area of metal-semiconductor contacts.

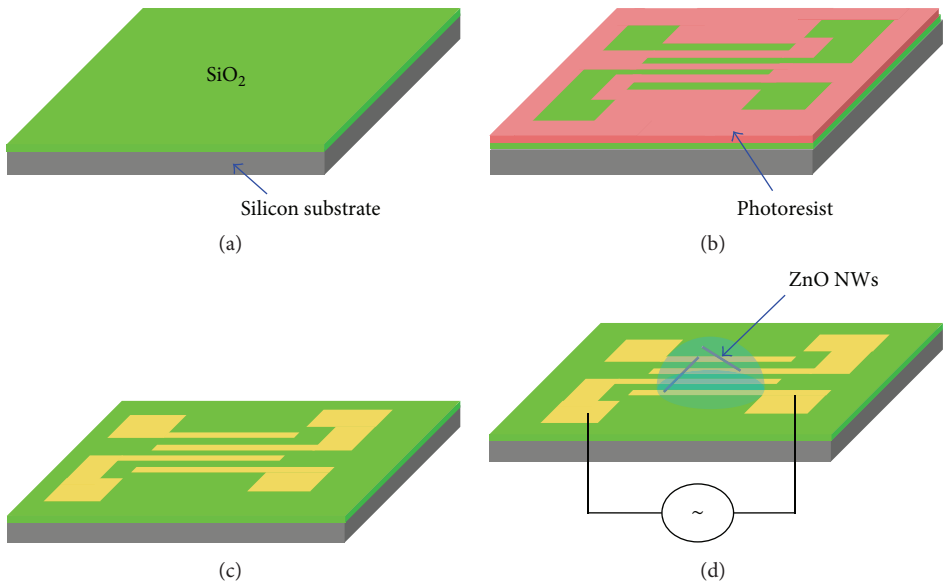

Figure 2: Diagrams of the fabricating procedure for a ZnO NW UV photodetector.

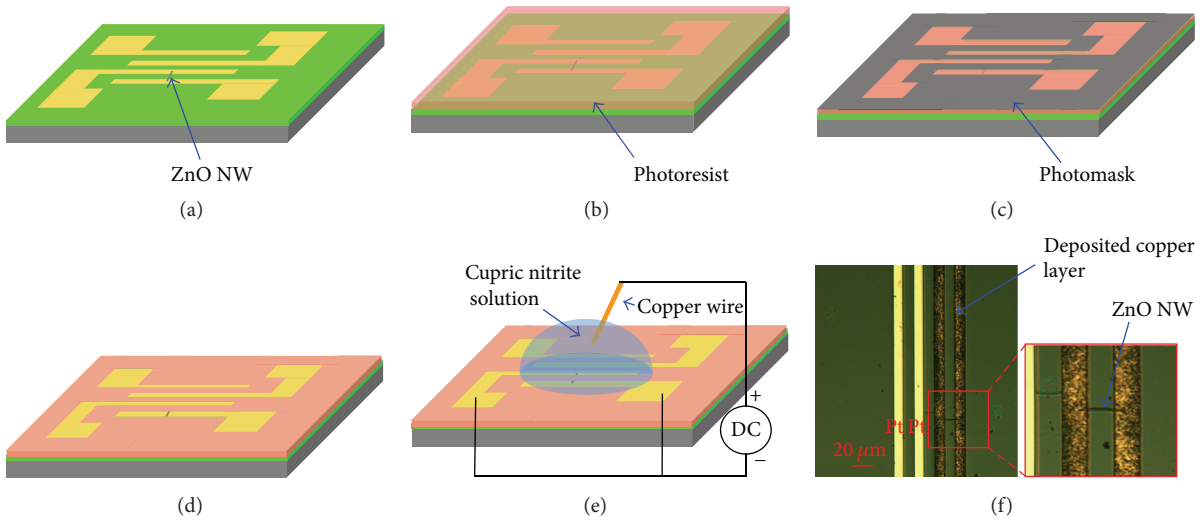

Figure 3: Diagrams of the lithography (a–d) and electrodeposition (e, f). (a) ZnO NW UV photodetector; (b) coat photoresist on the photodetector chip; (c) aligning and covering the photomask and exposure to UV light; (d) development of photoresist film; (e) electrodeposition of copper layer; (f) microscopy picture and diagram of the device.

4.2. Photoresponse Properties of the ZnO NW Photodetector. Figure 5 shows the time-dependent response curve of the ZnO NW photodetector without photoresist coating. The photocurrent increases steeply once the UV light is turned on. A few seconds later, the photocurrent increases slowly. The fast part of the curve may corresponds to the rapid photo-generated electron-hole pairs, and the slow part may correspond to the desorption process of oxygen from the surface of nanowires. When the light is off, the photocurrent declines very sharply at first; the current cannot decline to the initial value even after hundreds of seconds. These results suggest that desorption and reabsorption processes of oxygen from the nanowire surface are slow, which corresponds to the slow recovery speed of ZnO NW conductance.

To examine the effects of surface coating, we investigated the UV response characteristic of the device processed by spin-coating with photoresist. Figure 6 shows the results (the inset in Figure 6 is a schematic diagram of the ZnO NW photodetector). The resultant curve has an enhanced response and recovery speed compared to the result shown in Figure 5. When the UV light is on, the photocurrent has 20-fold increase in 3 s and then increased slowly in the next 20 s. When the UV illumination was off, the currents declined to initial levels within 20 s.

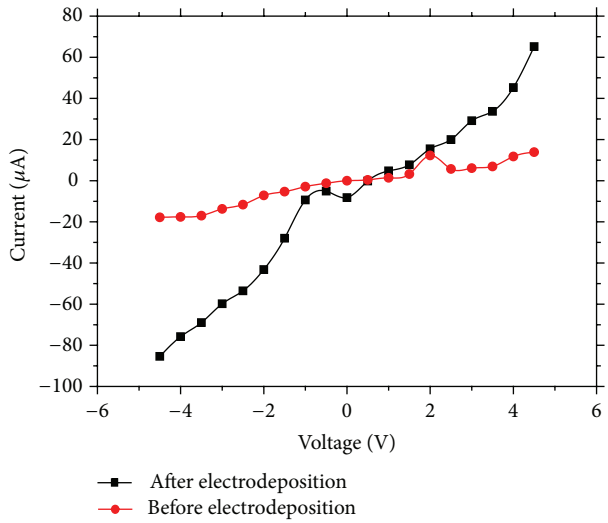

Figure 4: Comparison diagram of the *I-V* characteristics of the photodetector after (black)/before (red) electrodeposition.

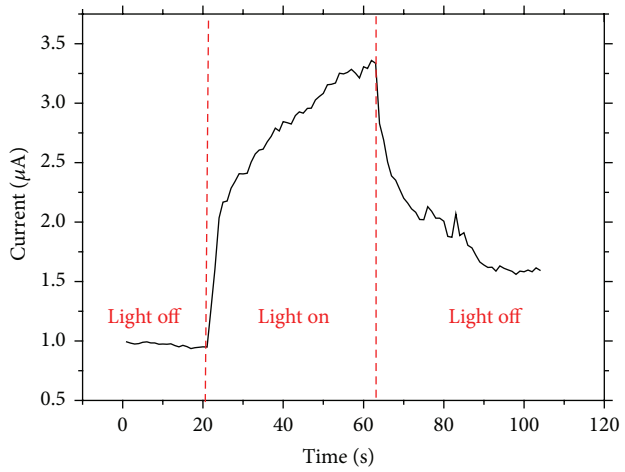

Figure 5: Time-related photoresponse characteristics of the ZnO NW UV photodetector without photoresist coating.

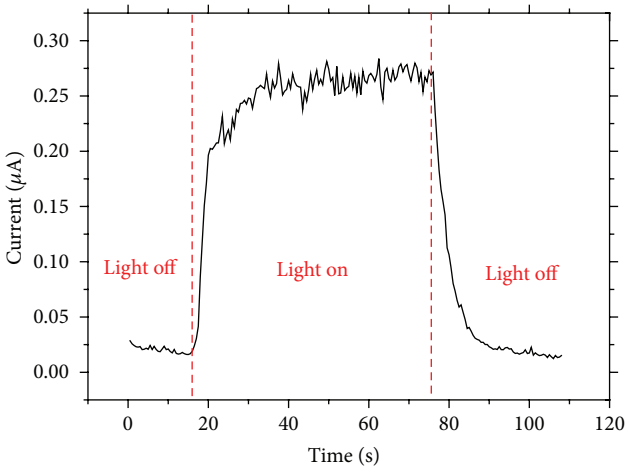

Figure 6: Time-dependent photoresponse characteristic of the ZnO NW photodetector with photoresist coating.

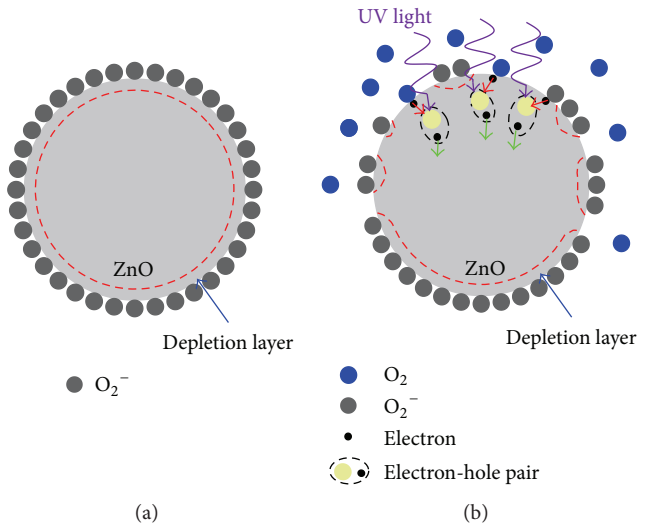

Figure 7: Schematic diagrams of the carrier transport mechanism of the ZnO NW (cross-section) without photoresist. (a) Oxygen molecules absorbed on the NW surface capture free electrons from the NW to generate O_2^-. A depletion region is formed under the surface of ZnO NW; (b) some O_2^- ions lose their electrons when the UV light illuminates the ZnO NW. The oxygen escapes from the surface of the nanowire.

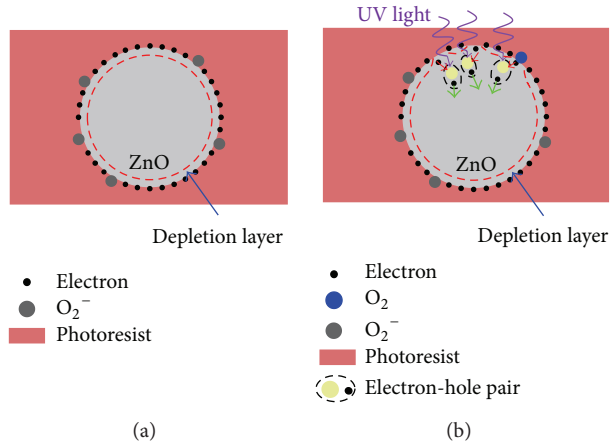

Figure 8: Schematic diagrams of the carrier transport mechanism of the ZnO NW (cross-section) with photoresist. (a) Photoresist and oxygen capture electrons from the NW and form a depletion layer below the surface of the ZnO NW; (b) photoresist and oxygen lose the electrons when the UV light illuminates the ZnO NW. Oxygen cannot escape the surface of the NW.

Comparing the results shown in Figures 5 and 6 reveals that the device coated with photoresist has a clear enhancement in response and recovery speed. This improvement indicates that surface coating can be an alternative method to enhance the response and recovery properties of the ZnO NW photodetector. Brief carrier transport mechanisms are illustrated in Figures 7 and 8.

When ZnO NW is exposed to the ambient atmosphere, oxygen is absorbed on the surface of the n-type ZnO NW. Then, oxygen captures the electrons to form O_2^- ions,

which subsequently form a depletion layer under the surface (Figure 7(a)) and induce a decrease in conductance of the ZnO NW. When the ZnO NW is illuminated by UV light (Figure 7(b)), the photo-generated electron-hole pairs enhance the conductivity of the ZnO NW by increasing the carrier density. The holes migrate to the surface of the ZnO NW and combine with the electrons absorbed on the surface. O_2^- loses an electron and is desorbed from the surface. When the UV light is off, the electron-hole pairs recombined fast; thus, the curve shows a sharp decline, as shown in Figure 5. But the physisorption speed of oxygen may be too slow to initialize the photocurrent; thus, the photocurrent cannot quickly recover to initial value.

The differences between ZnO NW devices with and those without photoresist are the absorption and desorption of oxygen, and the potential effects of photoresist are discussed. When the nanowires are coated by photoresist, the oxygen absorption and desorption may experience two effects (Figure 8(b)): the decrease of oxygen absorbing on the nanowire surface and the bound effects on absorbing oxygen induced by photoresist. Both effects can lead to the faster response and recovery time of the ZnO NW photodetector. At the same time, photoresist may have a similar effect on the ZnO NW to that of oxygen does. The difference exists in the illumination by UV light. Photoresist cannot be desorbed from the nanowire surface when it loses the electrons; thus, the electrons can rapidly transport to photoresist when the UV light was off. Thus, the rapid transfer of carriers occurs at the interface of the nanowire, and thus the photocurrent declines fast to initial value, as shown in Figure 6.

5. Conclusions

In this paper, we introduced a simple approach to process the ZnO NW photodetector by coating the nanowire with photoresist. The time-related response characteristics of the device with/without photoresist were measured to analyze the effect of photoresist. The ZnO NW photodetector had a clear enhancement in response and recovery speed after spin-coating with photoresist. This work also implements an electrodeposition process to improve the NW-electrodes contacts, which is ascribed to the lower work function of copper and the enlarged contact area of metal-semiconductor contacts. The results in this paper demonstrate that surface may be an effective and simple way to improve the response speed of photoelectric device which is susceptible to ambient atmosphere.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

Acknowledgments

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