Visible and ultraviolet light alternative photodetector based on ZnO nanowire/n-Si heterojunction

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Closely packed ZnO nanowire array was fabricated on a n-type Si (100) substrate by a magnetron cosputtering method. The ZnO nanowire/n-Si heterojunction showed good diode characteristics with rectification ratio of above $10^2$ at 4 V in the dark. Experiments demonstrated that the diode could be used to detect either visible or ultraviolet light by easily controlling the polarity of the voltage applied on the heterojunction. The spectral response of the device will be discussed in terms of the band diagrams of the heterojunction and the carrier diffusion process. © 2008 American Institute of Physics. [DOI: 10.1063/1.3003877]

As a wide band gap semiconductor, ZnO has drawn great attention in short wavelength laser diodes and ultraviolet (UV) photodetectors in recent years. ZnO has many advantages over other semiconductors as a photodetector material. It has been shown to be extremely resistant to high-energy proton irradiation.1 Furthermore, individual ZnO nanostructure has very high internal photoconductivity gain2 due to the surface-enhanced electron-hole separation efficiency. Therefore, ZnO nanostructures become a promising material to make UV detectors.

By now, many methods have been used to synthesize ZnO nanostructures, including chemical vapor deposition,3 metal-organic chemical vapor deposition,4 solution-grown 4,163501-3/$23.00 © 2008 American Institute of Physics microcrystalline method,5 sol-gel synthesis methods,6 electrochemistry deposition,7 physical vapor deposition,8 and laser-assisted growth methods.9 Most obtained ZnO nanostructure samples are with high density of interspaces between nanostructures. To make sensitive photodetectors, it is necessary to fill the interspaces with polymers or simply to use individual nanostructure to build a device.2,10 For the former, the contact between electrodes and ZnO may suffer due to the coating layer. For the latter, it is expensive and needs special equipments to make the device with nanosize. To improve the performance of the devices and to fabricate devices easily, it is essential to develop a method to grow closely packed ZnO nanostructures.

In this work, we adopted a direct current (dc) and radio frequency (rf) cosputtering method to fabricate closely packed ZnO nanowire arrays. In order to combine the potential advantages of one dimensional ZnO nanowires and the highly developed Si technology, a n-type Si (100) was used as a substrate. Interestingly, we succeeded in making a ZnO nanowires/n-Si heterojunction photodiode, which can detect either visible or ultraviolet light by applying forward or reverse bias on the device.

The cosputtering method includes a dc magnetron sputtering of a 99.999% pure Zn target under a power of 70 W and a rf magnetron sputtering of a 99.9% pure ZnO target under a power of 20 W. Before being loaded into the sputtering chamber, the silicon substrate was cleaned by organic solvents and etched in dilute HF acid to remove the contaminations and surface oxides. During the sputtering, a mixed gas of oxygen and argon with the same flow rate of 20 SCCM (SCCM denotes standard cubic centimeters per minute) was introduced into the chamber and the working pressure was maintained at 1 Pa. The substrate was kept at 400 °C with a rotation speed of 20 loops/minute and the growth time was 2 h. To make devices, 100 nm thick Au film was deposited on the ZnO nanowire arrays and 100 nm thick Al film was deposited on the back side of the n-type silicon substrate using evaporation method.

The morphology and the structure of the as-grown sample were investigated by field-emission scanning electron microscopy, energy-dispersive x ray (EDX), and x-ray diffraction (XRD). Current versus voltage (I–V) measurement was performed using a Hall measurement system. The photosresponse of the device was measured using a standard lock-in technique with a 150 W Xe lamp as an excitation light source.

Figure 1(a) shows the cross-sectional image of the ZnO nanowire arrays fabricated on the Si (100) substrate at 400 °C by the dc and rf cosputtering method. It reveals that all the ZnO nanowires grow vertically on the substrate. The surface morphology of the ZnO nanowire arrays shown in Figs. 1(b) and 1(d) prove that the nanowires are closely packed. From the magnified cross-sectional image in Fig. 1(c), the length of the ZnO nanowires can be measured to be about 500 nm. Also the root diameter of each single ZnO nanowire is smaller than the top diameter. The average diameter is determined to be about 40 nm. The EDX data shown in Fig. 1(e) indicate that the sample is consisted of O and Zn elements with more O atoms. The XRD pattern of the ZnO nanowire arrays fabricated on the Si (100) substrate is displayed in Fig. 1(f). The diffraction peak of the sample can be indexed to that of hexagonal wurtzite ZnO. Only the (002)
diffraction peak and the Si (400) can be observed, which indicates that ZnO nanowires are with perfect c-axis orientation. The full width at half maximum of the diffraction peak is 0.177°, suggesting the good crystallinity of the ZnO nanowire arrays. The detailed growth process of ZnO nanowires will be discussed elsewhere.11

The photodetector structure is sketched in Fig. 2(a). Au and Al were used as electrodes for ZnO and Si, respectively. When a forward bias was applied on the ZnO side, the I-V characteristic shown in Fig. 2(b) (black color) exhibits a good rectifying behavior with rectification ratio \( I_{\text{forward}}/I_{\text{reverse}} \) of above \( 1.6 \times 10^2 \) at 4 V in the dark, indicating the formation of a diode. The rectification ratio is much larger than that (~24) of molecular beam epitaxy grown ZnO-based heterojunction observed by Mandalapu et al.,12 which indicates that the electrical property of our magnetron sputtering heterojunction is quite good. The turn-on voltage and the reverse leakage current are found to be 2.58 V and \( 1.17 \times 10^{-7} \) A (at ~4 V), respectively. For the heterojunction, the current increases exponentially following the equation, \( I \sim \exp(\alpha V) \), which is usually observed in the wide band gap p-n diodes due to recombination-tunneling mechanism.13,14 The constant \( \alpha \) was evaluated to be 1.169 V\(^{-1}\) by fitting the experimental data in Fig. 2(b) (shown in red color), which falls in the range of 0.45−1.50 V\(^{-1}\) for the semiconductor junctions, as suggested by Fedison et al.12 The I-V characteristics between two as-deposited gold contacts on ZnO nanowire arrays is linear, indicating the formation of Ohmic contacts [Fig. 2(c)].15–17

Figure 3 shows the photocurrent spectra of the heterojunction irradiated from the ZnO nanowire array side when applying forward (red color) and reverse biases (green color). Interestingly, we only observed visible light response under forward bias and ultraviolet response under reverse bias. The wavelength of the decreasing edge under forward bias is about 375 nm, which corresponds to the cut off wavelength under reverse bias. The photoresponse mechanism of this heterojunction can be understood in terms of the energy band diagram based on Anderson’s model18 and the carrier diffusion process, as shown in Fig. 4(a). The band gap and electron affinity values are \( E_g \) \( \text{ZnO}=3.37 \) eV and \( X_{\text{ZnO}}=4.35 \) eV (Ref. 19) for ZnO and \( E_g \) \( \text{Si}=1.12 \) eV and \( X_{\text{Si}}=4.05 \) eV (Ref. 18) for Si, respectively. The model shows a small conduction band offset (0.3 eV) and a large valence band offset (2.54 eV). To understand the different spectral responses under forward and reverse biases, the energy band diagrams of the junction were also displayed in Figs. 4(b) and 4(c).

When a forward bias is applied on the ZnO nanowire array/n-Si heterojunction, the energy band diagram is de-
scribed as in Fig. 4(b). In this case, a visible light arriving at the junction will pass through the ZnO layer and be absorbed in the underlying n-Si to generate e-h pairs. These photogenerated electrons will pass through the barrier and drift toward ZnO side driven by the applied bias. Owing to the small conduction band offset value, a photocurrent signal can be obtained. When the heterojunction is illuminated by ultraviolet light, photons will be absorbed by the nanowires, generating carriers in the ZnO layer. The generated electrons are confined in the ZnO layer by the electric field. The generated holes cannot drift toward Si side to form current for its low mobility and short lifetime. Furthermore, it is easy to form a thin SiO₂ layer between Si and ZnO nanowire arrays at the beginning of the sputtering process as reported by Tan et al. which can easily block the movement of the holes. Therefore, no photocurrent signals will be detected in this case. Although the formed thin SiO₂ layer may also block the electrons under forward bias when a visible light irradiates, the much larger tunneling probability for electrons makes the heterojunction with good photoresponse. We find a fast decrease in photocurrent in the range of 400–350 nm because of the strong absorption of ZnO nanowire arrays. When the junction is negatively biased (a positive bias is applied on the Si side), the energy diagram is shown in Fig. 4(c). The visible light-generated electrons in Si cannot drift toward ZnO side owing to the reverse bias. The photogenerated holes are confined in the Si side because of the large valence band offset. As a result, no photocurrent is observed for visible light excitation. When an ultraviolet light shines on the junction, the ZnO nanowires will absorb the light and generate electrons and holes. Since the undoped ZnO usually exhibits a n-type conductivity, the photon-generated electrons will easily drift toward Si side, giving good photoreponse signal in the UV band.

In summary, ZnO nanowire array/n-Si heterojunction has been fabricated by a magnetron cosputtering method. The heterojunction showed a rectification ratio of above 1.6×10² at 4 V in the dark. A photodetector working in either visible or ultraviolet regions was achieved by applying forward or reverse biases on the heterojunction. We believe that this technique is very useful to integrate photodetectors with different cut off wavelengths on one chip.

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FIG. 4. The energy band diagram of the ZnO nanowire array/n-Si heterojunction under zero bias (a), forward bias (b), and reverse bias (c), respectively.