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ZnO nanowires array *p-n* homojunction and its application as a visible-blind ultraviolet photodetector

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We demonstrated a simple and low-cost fabrication of ZnO *p-n* homojunction. The junction consists of *n*-type ZnO nanowires array by a hydrothermal method covered with *p*-type Al, N co-doped ZnO film by a sol-gel method. The junction exhibits good rectification characteristics, with reverse leakage current and rectification ratio of ~5 μA and ~150 at bias of 3 V, respectively. The junction is operated as a photodetector when light radiation is shined on the glass-side of the device. The photodetector shows a peak responsivity at 384 nm with UV-visible responsivity ratio ($R_{384\ nm}/R_{550\ nm}$) of ~70 at an operating bias of −3 V. © *2010 American Institute of Physics*. [doi:10.1063/1.3299269]

Zinc oxide (ZnO) is an intrinsic semiconductor with a wide bandgap (≈3.37 eV at room temperature) and high exciton binding energy (≈60 meV). These properties have rendered ZnO a promising candidate for optoelectronic applications in blue and UV spectral range. Nonetheless, obtainment of *p*-type conductivity in ZnO remains a major challenge. The difficulty of making stable *p*-type ZnO films or nanostructures in a reproducible manner has impeded the development of ZnO *p-n* homojunction devices. Extensive efforts have focused on realizing *p*-type conductivity in ZnO films[1–5] and nanostructures.[6,7] Dopants like group I element Li,[2] and group V elements N (Refs. 3, 4, and 6) and P (Refs. 1, 5, and 7) have been attempted as acceptors of ZnO. Preparation of *p*-ZnO films has been reported by using magnetron sputtering,[1,2,5] which is relatively costly and requires high-temperature processes. To incorporate the processes into commercial-viable semiconductor device fabrication process, low temperature and low cost are important consideration. Attempts have been made to fabricate *p*-ZnO through sol-gel[3] and ultrasonic pyrolysis,[4] which require relatively lower cost and lower temperature. In this study, we fabricated ZnO *p-n* homojunction based on ZnO nanowires array prepared on optically transparent indium tin oxide (ITO) coated on glass substrates. The junction consists of hydrothermally grown *n*-type ZnO nanowires array covered with *p*-type Al, N co-doped ZnO film by a sol-gel method. The homojunction diode exhibits a high rectification ratio. In addition, it shows good photoresponse characteristics suitable for a favorable low-cost solution for visible-blind UV photodetector application.

The device fabrication is summarized as follows. ZnO nanowires array was first fabricated on ITO film on glass substrates by a commonly reported hydrothermal method.[8,9] The Al, N-codoped ZnO (AZO:N) film was then grown on the ZnO nanowires with a sol-gel method. The sol solution with zinc acetate dihydrate [$Zn(CH_3COO_2 \cdot 2H_2O)$], ammonium acetate [$CH_3COONH_4$], and aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 6H_2O$] in propan-2-ol was prepared, and stabilized by the addition of diethanolamine [$C_4H_{11}NO_2$]. The atomic ratio of Zn/N/Al is 1:1:0.02. The sol was spin-coated on the substrates, followed by sintering at 550 °C for 30 min. The whole spin-coating/sintering process was repeated several times to achieve a film thickness of about 200 nm. The device was finished by depositing 150 nm of Au on top of the AZO:N film via electron beam deposition. The final device was then heated at 300 °C for 15 min to improve device performance. The cross-section morphology of the junction was examined by scanning electron microscope (SEM) (Philips XL-30 FESEM). The absorption of the devices was measured by PerkinElmer Lambda 750 UV/VIS Spectrometer. The *I-V* characteristics of the devices were measured with Keithley 487 picoammeter/voltage source. Xe lamp (Newport 74000) equipped with a monochromator (Newport 66921) was used as the light source in the photoresponse measurment. A He–Cd laser source (325 nm) was used in the photoluminescence (PL) measurement.

A schematic diagram of the device is shown on Fig. 1(a). The ZnO nanowires array was first grown on ITO/glass substrate by a hydrothermal method commonly reported.[8,9] The

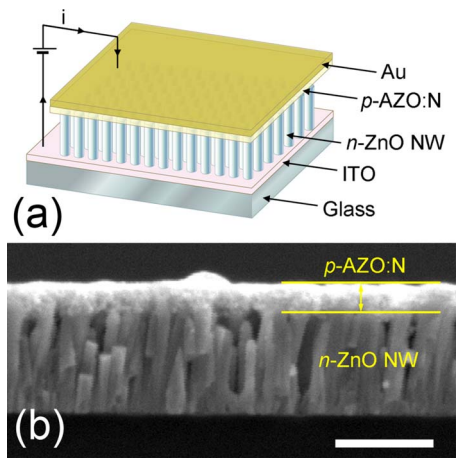

FIG. 1. (Color online) (a) Schematic diagram of the ZnO homojunction device. The circuit indicates that the device is connected with a positive bias. (b) An SEM image of the cross-section of the homojunction device. The scale bar is 500 nm.

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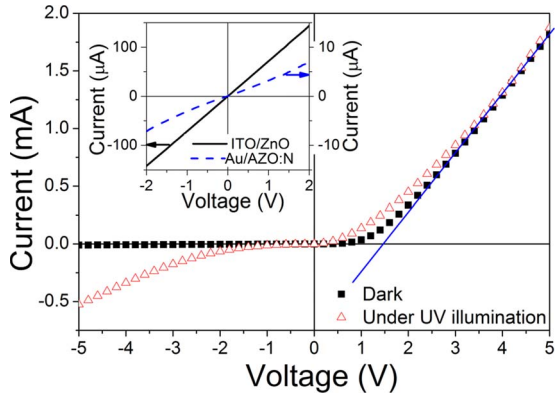

FIG. 2. (Color online) (*I-V*) characteristics of the homojunction device measured in the dark and under UV illumination (384 nm). The inset shows the *I-V* characteristics of the ITO/ZnO nanowires contact and the Au/AZO:N film contact.

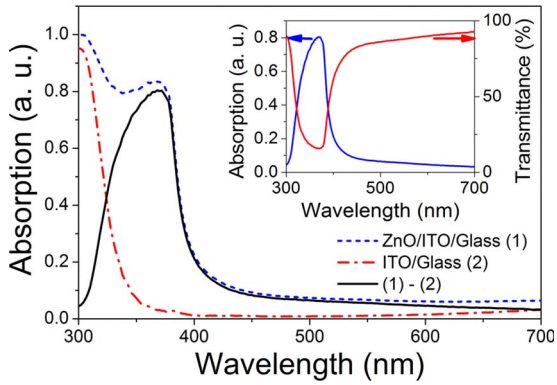

FIG. 3. (Color online) Absorption spectra of the whole device (1), only the ITO/glass substrate (2), and the measured absorption of the ZnO layers (1–2). The inset shows the absorption and the transmittance spectra of the ZnO layers.

diameter and length of the nanowires are ~50 and 500 nm, respectively. They are vertically-aligned and grow along the [0001] direction.[8,9] A layer of Al, N co-doped ZnO (AZO:N) film with thickness of about 200 nm was grown on the nanowires array by a sol-gel route. The AZO:N film was found to have *p*-type conductivity, with a carrier (hole) concentration of $\sim 10^{16}$ cm^{-3}, and mobility of 125–217 $cm^2\ V^{-1}\ s^{-1}$ by Hall measurement. Au was deposited as the anode. The junction area is about 0.25 cm^2. Figure 1(b) shows a cross-sectional SEM image of the homojunction. It can be observed that the nanowires are closely packed and the AZO:N film covers the nanowires thoroughly. The current-voltage (*I-V*) characteristic of the homojunction is shown on Fig. 2. The current increases nonlinearly with the forward bias, which indicates a *p-n* junction characteristic. The reverse leakage current and rectification ratio are ~5 μA (~20 $\mu A/cm^2$ for leakage current density if the junction area is taken into account) and 150, respectively at 3 V. We have fabricated over 20 devices, and 90% of them showed good rectifying behavior. Such behavior remained after the devices were exposed to the atmosphere for more than three months, indicating good device stability. It is supposed that the capping Au electrode would passivate the AZO:N film, and likely contribute to the stability. The *I-V* characteristics of both the ITO/ZnO nanowires and Au/AZO:N film contacts (inset of Fig. 2) are linear, showing that both contacts are Ohmic in nature. This in turn suggests that the rectifying behavior is related to the *p-n* junction. The turn-on voltage of the junction is about 1.5 V, which is smaller than the bandgap of ZnO (≈3.37 eV). The value is also smaller than the one reported in other *p-n* homojunctions reported.[1] The poor quality of the *p-n* junction accounts for this phenomenon. This is reasonable as both the ZnO nanowires array fabricated by hydrothermal method and the ZnO film by sol-gel method have modest crystal quality.[8,10,11] Upon UV illumination ($\lambda \approx 380$ nm, incident power ≈55 μW), the reverse current increases significantly with backward bias. At −3 V, the reverse current increases from ~5 μA in the dark to ~175 μA under UV illumination. On the contrary, the forward current does not increase as much, especially at higher bias.

When the device is operated as a photodetector, light is illuminated from the glass side. The light has to pass through the ITO/glass substrate before reaching the device. Thus, any interaction between the incident light and the ITO/glass substrate would vary the actual properties of the device. Figure 3 shows the absorption spectra taken on the whole device (1) and the ITO/glass substrate (2) only. It is observed that the ITO/glass substrate exhibits an absorption edge at about 350 nm. In other words, the ITO/glass substrate acts as a "low-pass filter" which absorbs light with wavelength below 350 nm. By subtracting the measured absorbance of the whole device by that measured on the ITO/glass substrate (1–2), we can observe an absorption plateau at wavelength of about 360–380 nm. This suggests that photodetectors with selectivity within that range can be realized. The transmittance of the device (inset of Fig. 3) remains relatively low at longer wavelengths. This is likely due to the scattering of light on the ZnO layers of the device.

To evaluate the performance and selectivity of the photodetector, the spectral photoresponse is studied. The spectral response of the detector with different biases is shown in Fig. 4. It can be observed that the cutoff wavelength is located at about 405 nm and the peak responsivity is located at about 384 nm with different biases. The cutoff wavelength (405 nm, $E \sim 3.06$ eV) is smaller than the band gap of ZnO (3.37 eV). This is likely attributed to poor crystal quality and the presence of band-edge defects in the ZnO layers. The responsivity at 384 nm increases from 2.5×10^{-2} A/W to 4 A/W as reverse bias increases from 0.1 V to 3 V. It should be noted that the responsivity peak at 384 nm is not commonly observed in most ZnO-based photodetectors reported. Such a

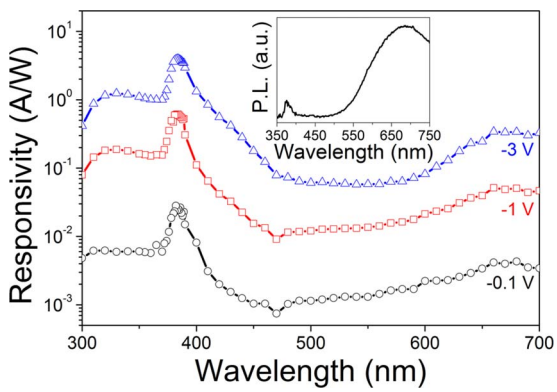

FIG. 4. (Color online) Photoresponse characteristics of the device at reverse bias of 0.1, 1, and 3 V. The inset shows the PL spectra of the ZnO layers under 325 nm excitation.

peak is contributed by two features of the device: the ZnO layer and the ITO/glass substrate. The ZnO layer absorbs light with energy close to its band gap while the ITO/glass substrate filters out light with higher energy, similar to the absorption plateau observed in Fig. 3. The photodetector also gives little response to light in orange/red spectral range. There is a small but broad response peak around 600–700 nm, which is likely due to the defects in ZnO. The broad peak is similar to the peak (at ~685 nm) observed in the PL spectra of the ZnO layers (inset of Fig. 4), which is attributed to the deep-level defects of ZnO.[8,10,12] The origin of the orange/red PL emission of ZnO is suggested to be associated to excess oxygen related defects.[8,10,12] Such kinds of defects may be originally present in the ZnO layers or introduced during the sintering/annealing processes.[11] Enhancement of red PL emission on ZnO by annealing in air has been reported previously.[10] The UV-visible responsivity ratio ($R_{384\ nm}/R_{550\ nm}$) is ~20 with a reverse bias of 0.1 V, and increases to ~70 with a bias of 3 V. Meanwhile, the UV to red ratio ($R_{384\ nm}/R_{670\ nm}$) is relatively low, with ~6 with a reverse bias of 0.1 V, and ~12 with a bias of 3 V.

In summary, we have demonstrated a simple and low-cost fabrication of ZnO *p-n* homojunction with good rectification characteristics. The reverse leakage current and rectification ratio are ~5 μA and 150 at bias of 3 V, respectively. The homojunction can act as a UV photodetector when light is shined from the glass side of the device. The photodetector shows a peak responsivity at 384 nm with UV-visible responsivity ratio ($R_{384\ nm}/R_{550\ nm}$) of ~70 at a bias of −3 V. The photodetector also shows a smaller response with red light (λ at 600–700 nm), which is likely due to the presence of deep-level defects in the material. This work suggests that efficient UV detectors based on ZnO can be fabricated with a simple, low-cost, and commercially-viable method. By improving the crystal quality of the ZnO layers, we expect that a highly efficient visible-blind UV detector can be realized.

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