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## ARTICLE

# A Self-powered ultraviolet detector based on a single ZnO microwire/p-Si film with double heterojunctions

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Recently, self-powered devices based on a p-n heterojunction were widely reported, but there were few reports about self-powered UV detectors based on a single ZnO microwire/p-Si film with double heterojunctions. Compared with the common p-n heterojunction type devices, the fabricated devices with double heterojunctions based on a single n-type ZnO microwire and a p-type Si film exhibited excellent electrical performance such as an ideal rectification behaviour and a low turn-on voltage. At zero bias, the fabricated device can deliver a photocurrent of 71 nA, a high photosensitivity of about  $3.17 \times 10^3$  under UV light ( $0.58 \text{ mW/cm}^2$ ) illumination and a fast rising and falling time of both less than 0.3 s. Furthermore, the photocurrent increased with the rising of the optical intensity at low power intensities. The physical mechanism has been explained by energy band diagrams.

## Introduction

As a representative and important II - VI group semiconductor with a direct wide-gap (a band gap of 3.37 eV) and a large excitation binding energy (60 meV), ZnO has become one of the promising photoelectric materials for photodetectors in the ultraviolet range<sup>1,2</sup>. In addition, ZnO can be easily synthesized and has a variety of crystal morphologies, such as nanowires<sup>3</sup>, nanorods<sup>4</sup>, nanobelts<sup>5</sup>, and nanotetrapads<sup>6</sup>. With high surface-to-volume ratio and high density of surface state, a monocrystalline ZnO nanowire/microwire can not only provide a direct passageway for electrons, but also increase the photoconductivity gain<sup>7</sup>. Except the application in UV detector, ZnO has many other exciting applications, such as electromechanical devices<sup>8,9</sup>, gas sensors<sup>10</sup>, field-effect transistors<sup>11,12</sup>, diodes<sup>13,14</sup>, and nanogenerators<sup>15,16</sup>. Nevertheless, all these devices mentioned above should work with external power sources, which increase the energy consumption. In recent years, research effort in the field of fabricating self-powered devices<sup>17</sup> has demonstrated the potential to build an independent, sustainable, and zero-maintenance nanodevices and nanosystems<sup>18</sup>. Among these devices, one attractive tendency is to use ZnO nano/microwire, to fabricate a detector that is self-powering, without battery or external power source<sup>19,20</sup>.

In the previous studies, there were mainly two types of junction in the photovoltaic self-powered UV detectors: the Schottky-barrier type<sup>21</sup> and the p-n junction type<sup>22</sup>. The built-

in electronic field in both contact type can separate the electrons and holes generated in depletion layer when the ultraviolet light focuses on the junctions. As compared with Schottky-barrier type devices, we have a keen interest in a p-n junction type devices. Since the required and reliable p-type ZnO was difficult and complicated, a variety of p-type materials, combined with n-ZnO to form heterojunctions, have been investigated, such as GaN<sup>23</sup>, PEDOT:PSS<sup>24</sup>, Si<sup>25</sup>. However, there were few reports about self-powered photodetectors with double heterojunctions based on individual n-type ZnO microwires and p-Si film.

In this paper, we fabricate a self-powered ultraviolet detector based on single ZnO microwire/p-Si film with double heterojunctions, which can not only work without the external bias, but also exhibited the outstanding electronic performance. Without external bias, the devices show a short response time of less than 0.3 s, excellent rectification behaviour, and a high photosensitivity of about  $3.17 \times 10^3$  under UV light ( $0.58 \text{ mW/cm}^2$ ) illumination. At low power intensities, the photocurrent exhibits a near-linear dependency on the intensity. The physical mechanism has been explained by the energy band diagrams. These results indicate that the fabricated self-powered devices with double heterojunctions can be used to build an independent, sustainable, and zero-maintenance self-powered nanodevices and nanosystems.

## Experimental methods

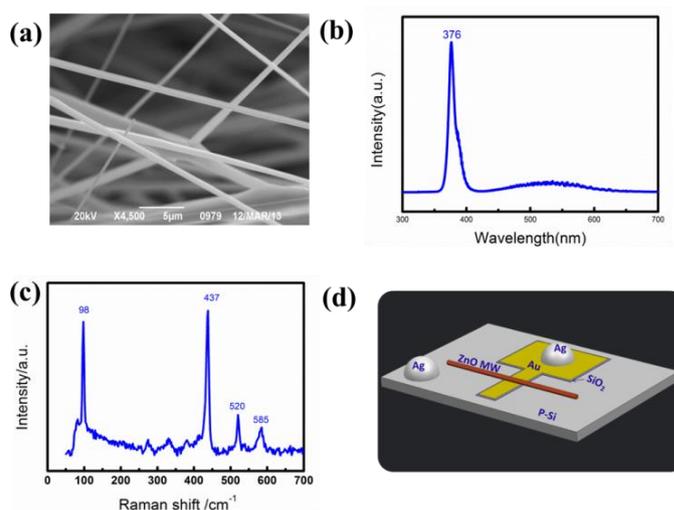
The ZnO microwires for our devices were synthesized through a conventional chemical vapour deposition (CVD) method. Firstly, Pure ZnO and C powder, used as the evaporation source and mixed with the same molar ratio, were placed in the bottom of a porcelain boat. A clean Si chip, covered on the boat, was used as the substrate for collecting sample. Subsequently, the boat was loaded on the middle part of the horizontal furnace for 20 min, where the reaction carried out at 950°C. Then the white products on the Si chip were ZnO wires with the same methodology.

To protecting the part from being sputtering insulator and metal, PE adhesive belt was pasted on specific part of the substrates. A SiO<sub>2</sub> layer with the thickness of 50nm and an Au layer with thickness of 30nm were sputtered on the substrates via magnetron sputtering. To fabricate the device, a single ZnO microwire of interest was transferred onto the prepared substrates by using a probe station under optical microscopy. The middle part of the ZnO MW was placed on the protuberant part of the substrate and two ends of the ZnO MW were contact with p-Si film with electrostatic interaction (in Figure 1 (d))

The morphology and structure of the ZnO wire and the fabricated devices were characterized by optical microscope and scanning electron microscope (FE-SEM, LEO1530). The electrical properties of the two kinds of photodetectors were tested at room temperature by using a semiconductor characterization system (Keithley 4200-SCS). A 355 nm laser was used as light sources and the laser power could be tuned by an attenuator.

## Results and Discussion

A typical SEM image of as-synthesized sample was depicted in Fig. 1 (a), from which it could be found that the width of ZnO wires were about several micrometers and the length is up to a hundred micrometers, with a smooth surface. Fig. 1 (b) displays the room-temperature photoluminescence spectrum of the ZnO wires. A sharp near-band-edge (NBE) emission peak centred at 376 nm and a weak green emission band around 500 nm were observed, implying the high crystal quality of the as-synthesized ZnO wires. Furthermore, to characterize the structure of the ZnO WMs, Raman spectra were taken at room-temperature, as illustrated in Fig. 1 (c). The strong Raman peaks at 98 and 437 cm<sup>-1</sup> are attributed to the non-polar E<sub>2</sub> vibration modes corresponding to the wurtzite phase. The slightly strong peak at 585 cm<sup>-1</sup> corresponded to E<sub>1</sub>(LO) mode and another peak at 520 cm<sup>-1</sup> was caused by the Si substrate. From the Raman spectra, the result confirms that the ZnO wires exhibit the high crystal quality, which was consistent with the result of PL spectra. To fabricate the n-ZnO wire/p-Si film hybrid structures with double heterojunctions (Fig. 1 (d)), a 50nm SiO<sub>2</sub> layer was used as insulating layer and a 50nm Au layer above the SiO<sub>2</sub> insulating layer was used to transferring electronic, acting as conducting layer. After that, the middle part of the as-grow ZnO MW was put on the protuberant part of the Au conducting layer, to fabricate ZnO microwire/p-Si film photodetector with double heterojunctions.



**Figure 1** (a) SEM image of ZnO MWs grown on the silicon substrate. (b) PL spectra of the ZnO MWs. (c) Raman spectrum of ZnO MWs and (d) Schematic diagram of the fabricated ZnO wire/p-Si film with double heterojunctions.

Fig. 2 (a) illustrates the SEM image of the fabricated ZnO wire/p-Si film detector with double heterojunctions. It can be found that the ZnO wire has a width of 25 μm and a length of about 1400 μm on each side contacting with the p-Si film. The *I-V* characteristics of the detector in dark (Fig. 2 (b)) revealed an excellent rectification ratio of about 300 at ±5V and a turn-on voltage of 2 V. The calculated ideality *n* for this heterojunction is about 3 from the intercept of the *dV/lnI* vs *I* curve in inset of Fig. 2 (b), according to the method *n* reported papers<sup>26</sup>. The forward *I-V* characteristic of a heterojunction in accordance with thermionic emission model, for  $V - IR_s > 3kT/q$ , is given by

$$I = I_s \exp\left[\frac{q}{nkT}(V - IR_s)\right] \quad (1)$$

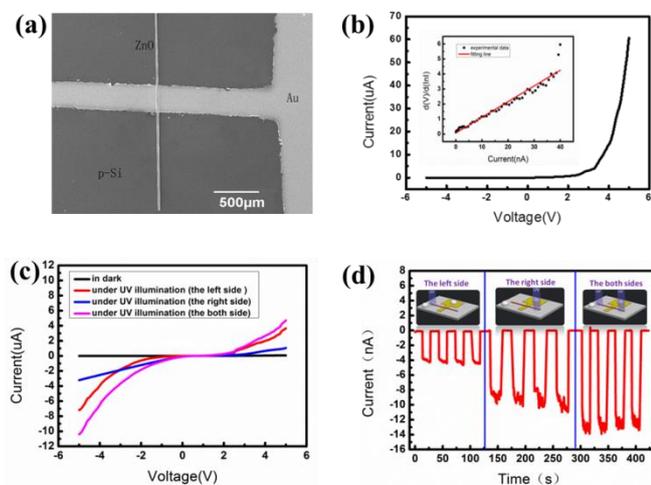
By differentiating Eq (1)

$$\frac{dV}{d \ln I} = \frac{nkT}{q} + IR_s \quad (2)$$

Where *k*, *T*, *R<sub>s</sub>* and *n* were Boltzmann's constant, absolute temperature, series resistance and ideality factor, respectively. For an ideal p-n junction, the ideality factor *n* should be 1 at low forward bias. Actually, the deviation of the calculated *n* from the ideal one is probably due to the presence of surface states, which provide multiple current pathways between the interfaces.

To investigate the photoelectric properties, we measured the curves of current versus voltage (*I-V*) in dark and under UV light (355nm) illumination, as shown in Fig. 2 (c). The enlarged image of the *I-V* characteristics under dark is displayed in Fig. 2 (b). The Au/ZnO contact reveals a neglected effect on the device transport behaviour, where only the pn junction determines the transport. When the UV laser focused on ZnO/p-Si heterojunctions on the left side, the right side and the both

sides respectively, the device all had highly responsive to UV light when the external bias increased from -5v to 5v, as illustrated in Fig. 2(c). In addition, it could be found that the device had much higher photocurrent when the both sides were illuminated by UV light. Interestingly, by turning off the bias source, whenever the UV light focused on ZnO/p-Si heterojunctions on the left side, the right side and the both sides respectively, the device also reveals a high photosensitivity (defined as  $I_{\text{light}} - I_{\text{dark}} / I_{\text{dark}}$ ) up to three order of magnitude, without external bias upon UV light, as shown in Fig. 2 (d). Furthermore, the photocurrent of both sides of the device under illumination of UV light was about sum of the left photocurrent and the right photocurrent. From the above-mentioned result, the designed device with double heterojunctions displayed more attractive self-powered function compared with a device with an n-type ZnO microwire/p-Si heterostructure. Increasing the area under UV illumination on one side means that the contact area between ZnO and P-Si would also be enlarged. The surface state of ZnO nanowires, particularly the small, yet measurable “green” defects as confirmed in PL spectra, will affect the separation and transport of photo generated carriers at the interface. As a result, these defects will trap carriers and reduce the conductivity in these detectors. In our experiments, on the other hand, the right side of the photodetector is outside the circuit as illustrated in Fig. 1(d). Once illuminated by UV source, only carrier would be injected into the circuit, thus would increase the carrier concentration and enhance the sensitivity. Furthermore, by alter the illumination location, opto controlled logic would be feasible, which needs further work.

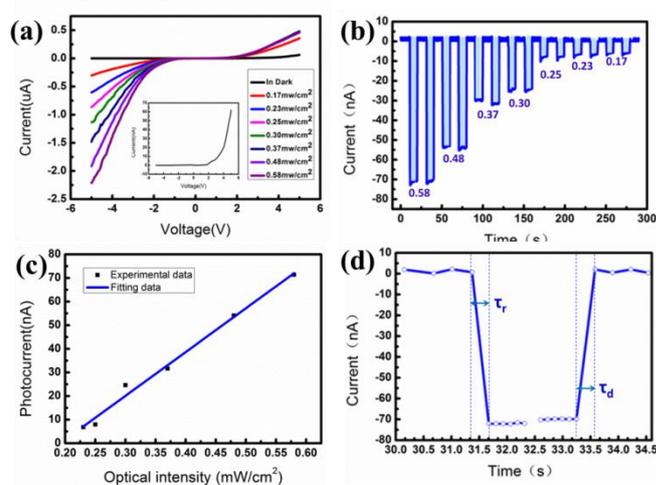


**Figure 2** (a) The SEM image of the fabricated ZnO wire/ p-Si film with double heterojunctions. (b)  $I$ - $V$  characteristics of the detector in dark. The inset shows the experimental and fitted  $dV/dI$  vs  $I$  plots used the  $I$ - $V$  curve in dark. (c)  $I$ - $V$  curves of the detector in dark and under illumination at UV (355nm) light (d) The current response curves of the detector upon UV light illumination being turned on and off at 0v bias.

The photocurrent of devices under UV illumination increased obviously with increasing the light intensities at reverse bias, while the devices were lowly responsive to UV light at forward bias (Fig. 3 (a)). The inset image was the

enlarged  $I$ - $V$  curve in dark, which showing an excellent rectification behaviour. The time response of the device exposed to different UV light intensities at 0V bias was shown in Fig. 3 (b). The photocurrent versus time under different laser illumination intensity being turned on and off was investigated in the same process. It could be found that the currents in dark were constant without normalization processing, indicating that the devices performed excellent stability and reproducibility. The photocurrent and photosensitivity of the devices at zero bias under ( $0.58\text{mW}/\text{cm}^2$ ) illumination was more than 7nA and  $3.17 \times 10^3$ , which is higher than that in reported devices<sup>21,24</sup>. Moreover, the square-wave curves demonstrated the devices had a short response time.

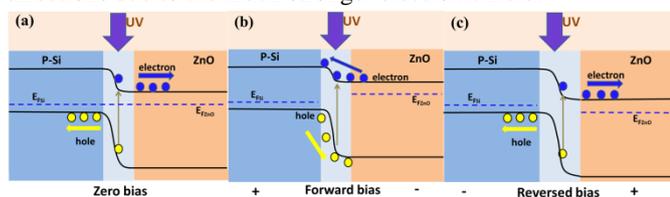
The experimental data and the fitting line of the photocurrents and light intensities were showed in Fig. 3 (c). The photocurrent showed a near-linear dependency on the intensity at low power intensities, because the photocurrent is proportional to the luminous flux with a constant carrier lifetime, which was consistent with the results in previous research<sup>27,28</sup>. Enlarged rising and falling parts of the current response under 355nm ( $0.58\text{mW}/\text{cm}^2$ ) UV illumination were displayed in Fig. 3 (d). The calculated response time of the device was about less than 0.3s, which was shorter than that of photoconductivity detectors based on ZnO wire reported in previous literatures (longer than 1s)<sup>29,30</sup>. Compared with the long response time of reported device based on hole-trapping mechanism, the rising and falling time of the designed devices were linear. The photo-generated electron-hole pairs could be quickly separated by the built-in electric field, leading to the rapid response speed.



**Figure 3** (a)  $I$ - $V$  curves of the devices in dark and under illumination of UV light with different light intensities. The inset shows the enlarged  $I$ - $V$  curve in dark. (b) Current-time curves of the devices at 0V bias upon on UV light with a series of intensities. (c) The light-intensity-dependent  $I_{sc}$  plots. (d) The enlarged rising and falling edges of the current response upon 365nm ( $0.58\text{mW}/\text{cm}^2$ ) illumination.

For the both sides of the devices with double heterojunctions, the energy band diagrams under illumination are the same. The energy band diagram of a p-n heterojunction on one side is investigated, as shown in Fig. 4. A depletion layer will be formed at the contact area when a ZnO wire is

placed on p-Si film. When the photon energy of UV light larger than the band gap at the interface, the electron-hole pairs will be generated in the depletion layer and the space charge region of the ZnO wire. However, the electron-hole pairs in the space charge region cannot result in an observed current at zero bias due to the high recombination rate<sup>[19]</sup>. However, the photon-generated electron-hole pairs in depletion layer can be quickly swept away from this area in opposite directions by the built-in electronic field at zero bias (Fig. 4 (a)), which can generate a larger photocurrent in a short time. Under forward bias (Fig. 4 (b)), the width of the depletion layer narrows (the height of barrier becomes low), and the generated electrons in space charge region of ZnO can transport through the depletion driven by the applied bias. In contrast, under reversed bias (Fig. 4 (c)), the width of the depletion layer shows to be larger, leading to the generated electrons and holes cannot pass across the barrier. In this case, the current in dark at reversed bias is much weaker than that at forward bias. But, when the UV light is focused on the device at reversed bias, the photocurrent will be much stronger than that at forward bias resulting from the photogenerated pairs can be swept away toward opposite directions due to the much stronger electronic field.



**Figure 4** The energy band diagrams of the fabricated n-ZnO MW/p-Si film heterojunctions under (a) zero bias, (b) forward bias, and (c) reverse bias, respectively.

## Conclusions

In conclusion, the newly designed device with double heterojunctions based on a single n-type ZnO microwire and a p-type Si film was reported. Compared to the rarely p-n heterojunction type device with an n-type ZnO microwire/p-Si heterostructure, the device with double heterojunctions displayed interesting electrical characteristics such as an excellent rectification of about 300 at  $\pm 5$ V and a low turn-on voltage of 2V. Under zero bias, the fabricated device can deliver a photocurrent of 71nA, a high photosensitivity of about  $3.17 \times 10^3$  under UV illumination and a fast rising and falling time both less than 0.3s. At low power intensities, the photocurrent exhibits a near-linear dependency on the intensity. The device of the double heterojunctions of n-ZnO microwire/p-Si might be a good candidate for potential applications in photodetection, sensors and photocatalysis.

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- S. Bai, W. Wu, Y. Qin, N. Cui, D. J. Bayerl and X. Wang, *Advanced Functional Materials*, 2011, 21, 4464-4469.
- D. Li, X. Sun, H. Song, Z. Li, H. Jiang, Y. Chen, G. Miao and B. Shen, *Applied Physics Letters*, 2011, 99, 261102.
- M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber and P. Yang, *Advanced materials*, 2001, 13, 113-116.
- Wang, C. J. Summers and Z. L. Wang, *Nano letters*, 2004, 4, 423-426.
- X. Y. Kong and Z. L. Wang, *Nano letters*, 2003, 3, 1625-1631.
- W. Wang, J. Qi, Z. Qin, Q. Wang, X. Sun and Y. Zhang, *The Journal of Physical Chemistry C*, 2012, 116, 12397-12400.
- C. Soci, A. Zhang, B. Xiang, S. A. Dayeh, D. P. Aplin, J. Park, X. Y. Bao, Y. H. Lo and D. Wang, *Nano letters*, 2007, 7, 1003-1009.
- S. Lu, J. Qi, Z. Wang, P. Lin, S. Liu and Y. Zhang, *RSC Advances*, 2013, 3, 19375.
- Y. Zhang, X. Yan, Y. Yang, Y. Huang, Q. Liao and J. Qi, *Advanced materials*, 2012, 24, 4647-4655.
- E. Comini, G. Faglia, G. Sberveglieri, Z. Pan and Z. L. Wang, *Applied Physics Letters*, 2002, 81, 1869.
- K. Keem, D. Y. Jeong, S. Kim, M. S. Lee, I. S. Yeo, U. I. Chung and J. T. Moon, *Nano letters*, 2006, 6, 1454-1458.
- H. T. Ng, J. Han, T. Yamada, P. Nguyen, Y. P. Chen and M. Meyyappan, *Nano letters*, 2004, 4, 1247-1252.
- Q. Yang, W. Wang, S. Xu and Z. L. Wang, *Nano letters*, 2011, 11, 4012-4017.
- S. N. Das, J.-H. Choi, J. P. Kar, K.-J. Moon, T. I. Lee and J.-M. Myoung, *Applied Physics Letters*, 2010, 96, 092111.
- P. X. Gao, J. Song, J. Liu and Z. L. Wang, *Advanced materials*, 2007, 19, 67-72.
- X. Wang, J. Song, J. Liu and Z. L. Wang, *Science*, 2007, 316, 102-105.
- W. Jin, Y. Ye, L. Gan, B. Yu, P. Wu, Y. Dai, H. Meng, X. Guo and L. Dai, *Journal of Materials Chemistry*, 2012, 22, 2863.
- Z. L. Wang, *Advanced Functional Materials*, 2008, 18, 3553-3567.
- S. Xu, Y. Qin, C. Xu, Y. Wei, R. Yang and Z. L. Wang, *Nature nanotechnology*, 2010, 5, 366-373.
- Z. Bai, X. Yan, X. Chen, H. Liu, Y. Shen and Y. Zhang, *Current Applied Physics*, 2013, 13, 165-169.
- Y. Yang, W. Guo, J. Qi, J. Zhao and Y. Zhang, *Applied Physics Letters*, 2010, 97, 223113.
- Y. Q. Bie, Z. M. Liao, H. Z. Zhang, G. R. Li, Y. Ye, Y. B. Zhou, J. Xu, Z. X. Qin, L. Dai and D. P. Yu, *Advanced materials*, 2011, 23, 649-653.
- W. I. Park and G. C. Yi, *Advanced materials*, 2004, 16, 87-90.

## Journal Name

24. Z. Wang, J. Qi, X. Yan, Q. Zhang, Q. Wang, S. Lu, P. Lin, Q. Liao, Z. Zhang and Y. Zhang, *RSC Advances*, 2013, DOI: 10.1039/c3ra42778a.
25. J. J. Hassan, M. A. Mahdi, S. J. Kasim, N. M. Ahmed, H. Abu Hassan and Z. Hassan, *Applied Physics Letters*, 2012, 101, 261108.
26. S. K. Cheung and N. W. Cheung, *Applied Physics Letters*, 1986, 49, 85.
27. Z. Fan, H. Razavi, J. W. Do, A. Moriwaki, O. Ergen, Y. L. Chueh, P. W. Leu, J. C. Ho, T. Takahashi, L. A. Reichertz, S. Neale, K. Yu, M. Wu, J. W. Ager and A. Javey, *Nature materials*, 2009, 8, 648-653.
28. K. S. Stevens, M. Kinniburgh and R. Beresford, *Applied Physics Letters*, 1995, 66, 3518.
29. Y. Jin, J. Wang, B. Sun, J. C. Blakesley and N. C. Greenham, *Nano letters*, 2008, 8, 1649-1653.
30. W. Kim and K. S. Chu, *physica status solidi (a)*, 2009, 206, 179-182.