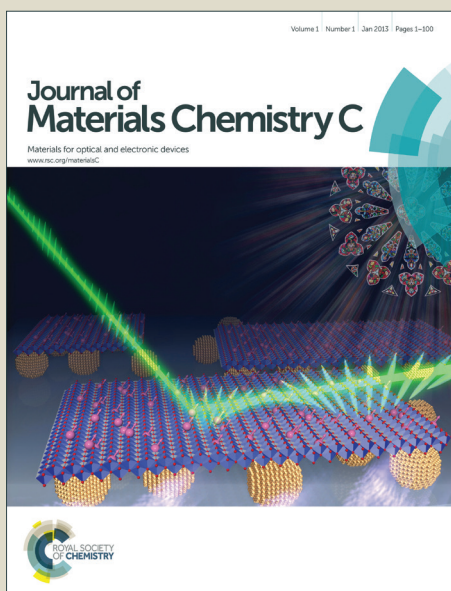


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Realization of self-powered ZnO MSM UV photodetector with high responsivity using asymmetric pair of Au electrodes

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Received Xth XXXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXXXX 200X

DOI: 10.1039/b000000x

We demonstrate a novel type of ZnO self-powered photodetector based on the asymmetric metal-semiconductor-metal (MSM) structure: one Au interdigitated electrode with wide fingers and the other one with narrow fingers. These ZnO photodetectors exhibit an attractive photovoltaic characteristics at zero bias voltage. More interestingly, with increasing the asymmetric ratio (the width of wide fingers/the width of narrow fingers) of the interdigitated electrodes, the responsivity of ZnO self-powered UV photodetectors was enhanced obviously, and it could reach as high as 20 mA/W when the asymmetric ratio is 20:1. A physical model based on band energy theory was developed to illustrate the origin of the photoresponse at 0 V in our device. Our findings provide a new route to realize the self-powered photodetectors.

Introduction

Ultraviolet photodetector has drawn extensive attention due to their broad applications, including missile plume sensing, flame detection, convert space-to-space communication, and water purification, etc..^{1–6} From an application point of view, the UV photodetectors operating without any power supply, namely self-powered photodetectors, have some special advantages, such as saving energy, small device size, and suitable use in extreme conditions. Thus, the self-powered UV photodetectors have recently received an increasing attention. Till now, p-n junction, Schottky junction, and heterojunction have been widely used to realize this type of devices due to their efficient separation ability of photo-excited electron-hole pairs by photovoltaic effect.^{7–15}

In the past several decades, ZnO has been investigated for photodetectors in the UV range due to its wide direct band gap (~ 3.37 eV), low defect density, and strong radiation hardness.^{4,5,16,17} However, owing to the lack of high quality and stable p-ZnO, very little information is available regarding the ZnO p-n homojunction photodiodes. Although some self-powered ZnO UV photodetectors have been demonstrated based on vertical Schottky junction and heterojunction, it still exists many problems in these devices, such as the complicated preparation process and the poor electrode contacts in vertical Schottky photodiodes. As for heterojunction, the large lattice mismatch between ZnO and other materials could strongly degrade the device performance. Therefore, the existed self-powered ZnO photodetectors usually have a poor performance, and a new type of self-powered UV photodetector with high responsivity is urgently needed.

Till now, most of ZnO-based photodetectors are based on the metal-semiconductor-metal (MSM) structures, which are controllable, stable, and can be fabricated easily. However, the traditional MSM photodetectors always require the external power source as the driving force to generate photocurrent due to their two symmetric Schottky contacts connected back-to-back on a planar surface.^{4,18–22} According to the previous reports, MSM devices using different materials as two electrodes (one is Ohmic contact and the other is Schottky contact) could be recognized as planar Schottky photodiodes, which can be operated at zero bias voltage.²³ However, just like the vertical Schottky photodetector, the fabrication process of MSM devices with two different electrode materials is complex, and their performance is still not very high. Recently, it is found that the size of metal electrode can strongly affect the distribution of electric field built in the Schottky junction.^{24–27} As is well known, the electric field can prevent recombination of photo-generated electro-hole pairs, and efficiently separate the photo-generated carriers. Therefore, the self-powered ZnO MSM photodetector is expected to be realized by using the asymmetric pair of planar electrodes.

In this article, we demonstrated a novel ZnO self-powered UV photodetector with the asymmetric MSM structure: one

† Electronic Supplementary Information (ESI) is available. See DOI: 10.1039/b000000x/

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Au interdigitated electrode with wide fingers and the other one with narrow fingers. Interestingly, once the finger width of wide electrode is fixed, the responsivity could be significantly enhanced by decreasing the finger width of narrow electrode. The responsivity at the wavelength of 365 nm without any external power supply can reach as high as 20 mA/W and this value is higher than that of previous reported ZnO-based self-powered photodetectors.^{8,28–31} A physical model based on band energy theory was developed to illustrate the origin of the photoresponse at 0 V in our ZnO self-powered photodetectors.

Experimental Section

In order to fabricate the self-powered ZnO detector. ZnO layers are employed as the active layers of the detector, and they are grown on *a*-plane sapphire substrate in a VG V80H plasma-assisted molecular-beam epitaxy (MBE) system. Prior to growth, the sapphire substrate was pretreated at 800 °C for 30 min to remove any possibly adsorbed contaminants and produce a clean surface. High-purity (6 N) elemental zinc was used as the precursor for the growth, and the oxygen source used was radical oxygen produced in a plasma cell operating at 300 W. The pressure in the growth chamber during the growth was fixed at 2×10^{-3} Pa. Firstly, ZnO buffer layer were deposited onto the *a*-plane sapphire substrate at 400 °C for 6 min, then increase to 750 °C for 120 min, and ~ 500 nm ZnO layers were epitaxied. After that, the asymmetric Au interdigital electrodes were patterned using a photolithography process.

The structure and the morphology of ZnO films were characterized by scanning electron microscope (SEM; Hitachi, S-4800), atomic force microscope (AFM) and X-ray diffractometer (Bruker D8X). A Hall measurement system (Lake Shore HMS7707) and a Keithley 2611A Source Meter were employed to investigate the electrical properties. The spectral response and the time resolved response of the photodetector were measured by a 150 W Xe lamp, monochromator, chopper, lock-in amplifier, and a YAG: Nd laser (266 nm), respectively.

Results and Discussion

Fig. 1(a) shows the SEM image of the as-grown ZnO film, and the inset is the high-resolution picture. It can be found that the ZnO film is uniformly fabricated on *a*-plane sapphire with relatively smooth surface. To further investigate the surface property of ZnO film, the topographies of the ZnO epilayer was characterized by typical tapping-mode AFM. As shown in Fig. 1(b), the average rms roughness of the ZnO film is calculated to be ~ 2.8 nm. The structural characterizations of the

ZnO films were assessed by x-ray diffraction (XRD) [see Fig. 1(c)]. Besides the diffraction from the substrate, only one peak at 34.44° can be observed from the XRD pattern, which can be indexed to the diffraction from the (0002) facet of wurtzite ZnO. The XRD result indicates that the ZnO layer has crystallized in hexagonal wurtzite structure with *c*-axis preferred orientation. The X-ray rocking curve of the ZnO film is displayed in the inset of Fig. 1(c), and a Gaussian lineshape with a full width at half maximum (FWHM) of around 0.22° can be observed. In addition, the phi-scan was employed to further analyse the in-plane orientation of the ZnO film, as shown in Fig. 1(d). Six sharp Phi-scan peaks of the ZnO at 60° interval confirm that the epitaxial ZnO exhibits a single-domain wurtzite structure with hexagonal symmetry.

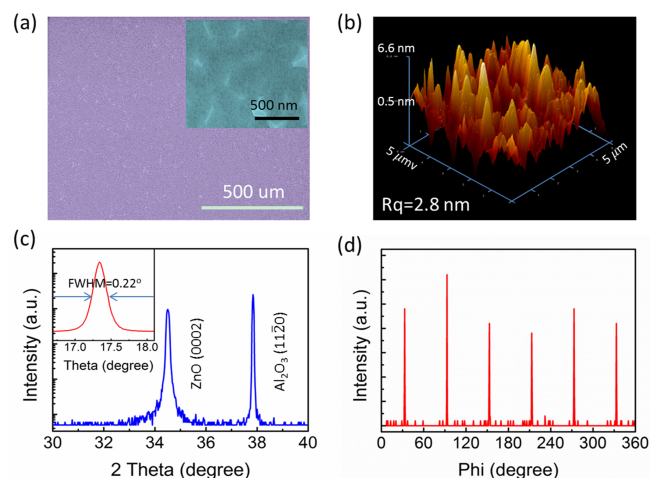


Fig. 1 (a) Low/high magnification SEM, and (b) AFM images of ZnO film. (c) XRD pattern of ZnO film. The inset shows its X-ray rocking curve. (d) X-ray phi-scan spectrum of the ZnO film.

Fig. 2 is the schematic illustration of ZnO MSM UV photodetectors based on the above mentioned films. 12 pairs interdigital metal electrodes with $500 \mu\text{m}$ length and $10 \mu\text{m}$ gap were formed by a 40 nm thick Au layer. In order to investigate the size effect of metal electrodes on the performance of ZnO MSM photodetectors, one electrode (Au#1) finger width (w_1) was fixed at $100 \mu\text{m}$, while the other electrode (Au#2) finger width (w_2) varies between $5 \mu\text{m}$ and $100 \mu\text{m}$. The devices with w_2 of 5, 10, 25, 50, and $100 \mu\text{m}$, are labeled as S1, S2, S3, S4, and S5, respectively.

Fig. 3(a) shows the photoresponse spectra of the aforementioned 5 photodetectors at 0 V bias. It can be found that all the detectors based on the asymmetric Au interdigitated electrodes structure exhibited an attractive photovoltaic characteristic. More interestingly, with the decrease in w_2 from $100 \mu\text{m}$ to $5 \mu\text{m}$, the asymmetric ratio of the interdigitated electrodes ($w_1:w_2$) increases from $\sim 1:1$ to $20:1$ and the responsivity could be enhanced significantly. For S1 (asymmetric

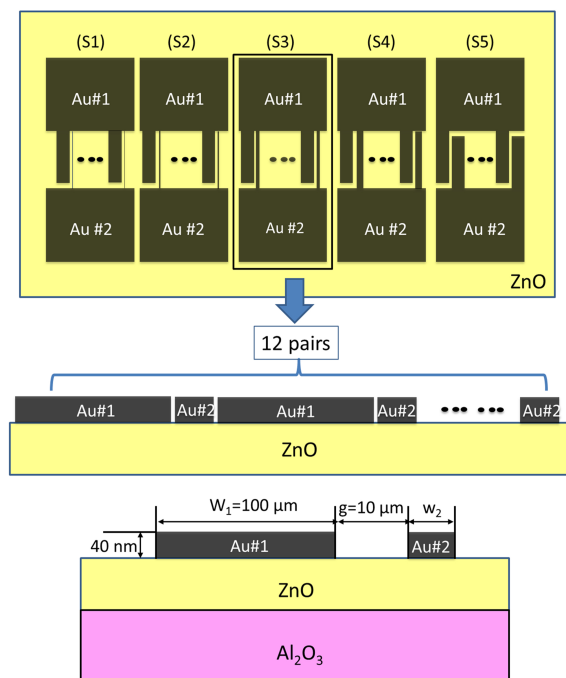


Fig. 2 Schematic illustration of the self-powered ZnO detector.

ratio = 20:1), the maximum responsivity can reach as high as ~ 20 mA/W, which is the highest value ever reported for ZnO-based self-powered photodetectors, including p-n junction, metal-oxide-semiconductor structure, Schottky junction and hetero-junction (See Tab. 1). A sharp cut off of responsivity can be seen at the wavelength of ~ 375 nm, corresponding to the band gap energy of ZnO. In addition, the UV-visible rejection ratio $[R(365 \text{ nm})/R(400 \text{ nm})]$ is more than 2 orders of magnitude. The sharp cut off edge and the relatively high UV-visible rejection ratio at 0 V indicate that our device is a high-performance intrinsic visible-blind self-powered UV photodetector.

As mentioned above, one advantage of the self-powered devices is that they are suitable for long-time operation in extreme conditions, and thus the reliability of these devices should be very important. As shown in Fig. 3(b), the responsivities of the detectors were nearly constant during the 120 days, indicating the high reliability and stability of our self-powered photodetectors. To further characterize our photodetector, the illumination intensity-dependence of the photocurrent is measured under a UV light (365 nm). In Fig. 3(c), as the illumination intensity increases from $30 \mu\text{W}/\text{cm}^2$ to $310 \mu\text{W}/\text{cm}^2$, the photocurrent increases nonlinearly, suggesting a complex process of electron-hole generation, recombination, and trapping in our device.

The temporal photoresponse of ZnO self-powered UV photodetector was measured at 0 V with a pulsed YAG: Nd laser as

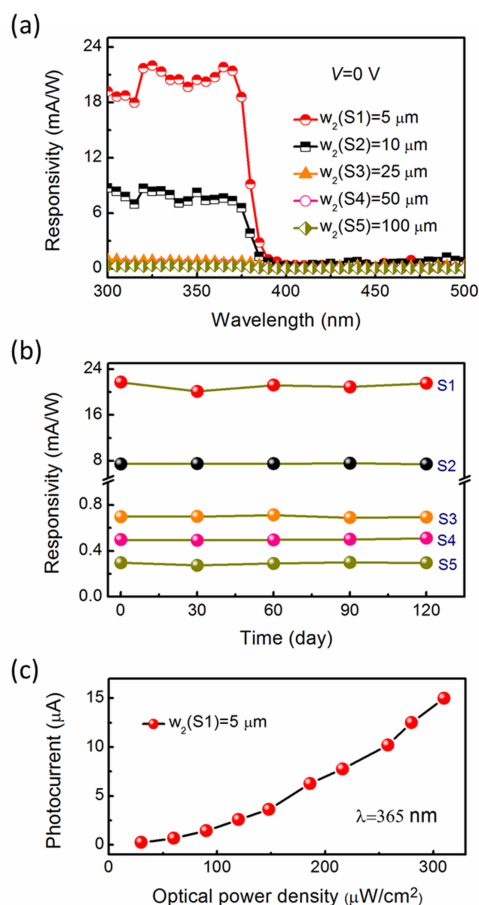


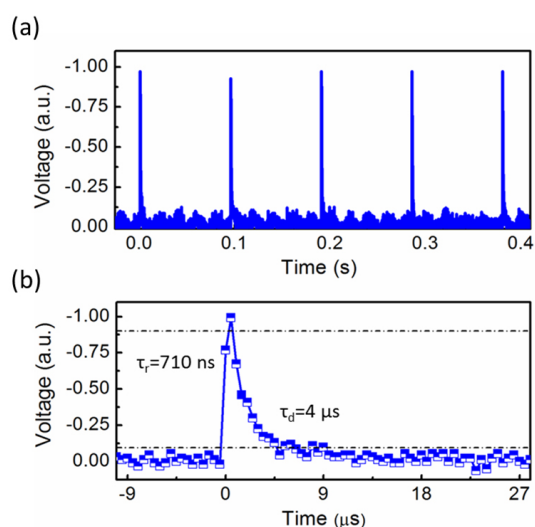
Fig. 3 (a) Spectral photoresponse of the ZnO photodetectors at 0 V bias. (b) The responsivity at 365 nm as a function of time. (c) Light-intensity dependence of the photocurrent at 365 nm.

the optical source (The laser pulse width was 10 ns and the frequency was 10 Hz), and the measurement setup was shown in Fig. S1. As shown in Fig. 4(a), the photoresponse of our self-powered device was very fast, highly stable and reproducible. The 10-90% response time (τ_r) and decay time (τ_d) are measured to be ~ 710 ns and $\sim 4 \mu\text{s}$, respectively [see Fig. 4(b)]. In addition, considering the negative photo-induced voltage and the measurement configuration, the potential of Au#1 is higher than that of Au#2 under UV illumination for S1.

To explore the origin of such an attractive photovoltaic characteristic in these detectors, I - V characteristics measurement was carried out on the asymmetric MSM (Au#1-ZnO-Au#2) detectors. The left in Fig. 5(a) is the schematic illustration of configuration for measuring the I - V characteristic and the right is the optical image of five devices fabricated on one large ZnO film. As illustrated in Fig. 5(b), the contact between Au and ZnO is a typical Schottky contact for all devices. Moreover, with decreasing w_2 from $100 \mu\text{m}$ to $5 \mu\text{m}$, the transition from

Table 1 Comparison of the characteristic parameters of the ZnO-based self-powered photodetectors obtained in the present work and previous.

Devices	materials and structures	Responsivity at 0 bias voltage (mA/W)	UV-visible rejection ratio	ref.
Asymmetry MSM	Au _{#1} -ZnO-Au _{#2}	20	10 ²	this work
p-n junction	p-ZnO(Li,N)/n-ZnO	0.018	-	28
Hetero-junction	p-GaN/n-ZnO	0.001	10	8
MS	Au/MgZnO	0.059	<10 ²	29
MIS	Au/ZnO(i)/ZnO(n)/In	0.03	-	30
MOS	Au/MgO/MgZnO	11	-	31

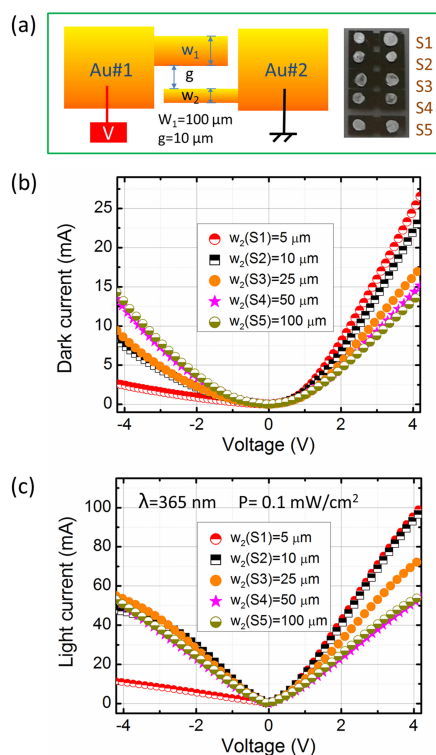
**Fig. 4** (a) and (b) Time-resolved response of the photovoltage of device (S1) at the applied bias of 0 V.

a symmetric to an asymmetric profile of the I - V curves can be observed between the positive and negative voltage regions. In general, for a Schottky contact, if $E_{00} \ll k_B T$, the thermionic emission is dominated in the junction electronic transport process without tunneling, where k_B is the Boltzmann constant, T is absolute temperature, E_{00} is the characteristic energy related to the tunneling probability.^{32–35} E_{00} can be expressed by following formula:

$$E_{00} = (q\hbar/2)(N/m^*\epsilon_s)^{1/2} \quad (1)$$

where q is the elementary charge, \hbar is the reduced Planck constant, N is the carrier density, m^* is the effective mass and ϵ_s is the relative dielectric permittivity. In this work, $m_e = 0.27 m_0$, and $\epsilon_s = 8.3$ for ZnO, and the carrier concentration N is about $9.3 \times 10^{16} \text{ cm}^{-3}$. E_{00} is about 2.2 meV for the ZnO films, which is much smaller than the thermal energy $k_B T$ at room temperature (26 meV). Thus, the current passing through the Schottky barrier can be described as following:

$$I = I_0 \exp(qV/nk_B T) [1 - \exp(-qV/k_B T)] \quad (2)$$

**Fig. 5** (a) Schematic illustration of configuration for measuring the I - V characteristic and optical image of the devices. (b) I - V characteristics of the asymmetric MSM (Au_{#1}-ZnO-Au_{#2}) photodetectors in dark. (c) I - V characteristics of the photodetectors under UV illumination at the wavelength of 365 nm.

$$I_0 = AA^* \exp(-q\Phi_B/k_B T) \quad (3)$$

Where k_B is Boltzmanns constant, T is the absolute temperature, n is the ideality factor, A is the junction area, A^* is the Richardson constant ($A^* \equiv 4\pi m^* q^2 / h^3$), Φ_B is the barrier height, h is the Planck constant, and I_0 is the reverse saturation current. Based on the thermionic model, I_0 could be derived from the I - V curves of the photodetectors in Fig. 4(b). By the calculation using Eqs. (2) and (3), it can be concluded that the Schottky barrier height in all devices is around 0.8 eV.

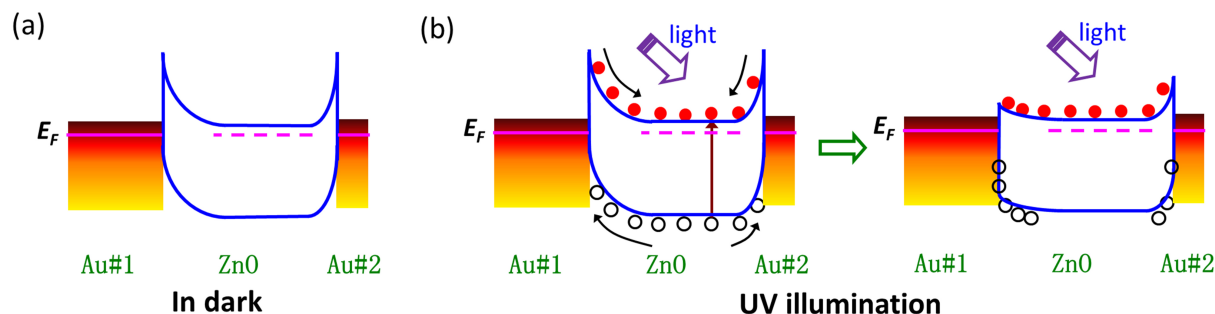


Fig. 6 Energy band diagrams of the asymmetric MSM photodetector at 0 V: (a) In dark (b) Under UV light.

This means that the Schottky barrier between Au and ZnO is independent of the size of electrodes. The reason for this phenomenon is that the Schottky contact between Au and ZnO is determined by their work function and interface states.³⁶

In order to better understand the mechanism of the photoresponse at 0 V of our devices, a model based on energy band theory was proposed as shown in Fig. 6. Schematics of the energy band diagrams in dark and under UV illumination are displayed in Figs. 6(a) and 6(b), respectively. In the dark, the Schottky barriers with a barrier height of ~ 0.8 eV are formed at the Au#1/ZnO and Au#2/ZnO interfaces, where Au electrodes and ZnO have the same Fermi energy level (E_F). According to the theory calculations (Ref. 24-26 and Fig. S2), the width of depletion region at Au#1/ZnO interface should be larger than that at Au#2/ZnO interface [see Fig. 6(a)]. Under UV illumination, electro-hole pairs are generated in ZnO as shown in Fig. 6(b). The generated electrons in the conduction band (CB) tend to move away from the contact, while the holes in the valence band (VB) tend to move close to the interface toward the metal side. The accumulated and trapped holes at the interfaces modify the local potential profile, so that the effective height of the Schottky barriers is lowered.³⁷⁻³⁹ Due to the difference in the width of depletion layer between Au#1/ZnO and Au#2/ZnO, the asymmetric electric potential distribution in ZnO film could induce the difference in the carriers separation and transport. Thus, the number of the accumulated and trapped holes at two interfaces is different, which induces the difference in the decrease of the Schottky barrier height between Au#1/ZnO and Au#2/ZnO. As a result, a typical photovoltaic characteristic can be observed in asymmetric MSM photodetectors at 0 V bias voltage. It must be mentioned here that the barrier height change is strongly dependent on the electrical properties of ZnO and the structure of Au electrodes, which could determine the direction of photovoltage. As for the traditional MSM photodetectors, the structure of two symmetric electrodes can not produce any photoresponse without the power supply.^{4,7,17,20,22,32,40} It is worth mentioning that the

S5 with the symmetric interdigital electrodes also has the responsivity at 0 V in our experiment, it is mainly caused by the experimental errors (see Fig. S3).

Conclusions

In summary, the self-powered ZnO UV photodetectors were firstly realized by using the asymmetric pair of planar electrodes. The responsivity at 0 V was significantly enhanced by increasing the asymmetric ratio between two electrodes, and could reach as high as 20 mA/W with the asymmetric ratio of 20:1. This value is higher than that of other kinds of self-powered ZnO-based photodetectors such as p-n junction, Schottky junction, and hetero-junction. The origin of the photoresponse at 0 V in our devices should be associated with the asymmetric electric potential distribution in ZnO film and the accumulated and trapped holes at the Au/ZnO interfaces. In addition, due to its advantage of relatively simpler fabrication technology, this asymmetric MSM structure should be an excellent choice to obtain high-efficiency self-powered ZnO UV photodetectors, and this method can also be extended to the devices based on other semiconductor materials.

Acknowledgments

The authors thank Dr. Jian-Wei Zhang and Dr. Deng-Kui Wang for their technical assistances and kind help. This work is supported by the National Basic Research Program of China (973 program) (Nos.2011CB302006), the National Natural Science Foundation of China (Nos.10974197, 11174273, 11104265, 11134009, 61376054), the 100 Talents Program of the Chinese Academy of Sciences.

References

- Z. Xu and B. M. Sadler, *IEEE Commun. Mag.*, 2008, **46**, 67-73.
- Y. Taniyasu, M. Kasu and T. Makimoto, *Nature*, 2006, **441**, 325-328.

- 3 E. Gorokhov, A. Magunov, V. Feshchenko and A. Altukhov, *Instrum. Exp. Techn.*, 2008, **51**, 280–283.
- 4 L. Wang, Z. Ju, J. Zhang, J. Zheng, D. Shen, B. Yao, D. Zhao, Z. Zhang, B. Li and C. Shan, *Appl. Phys. Lett.*, 2009, **95**, 131113.
- 5 K. Liu, M. Sakurai and M. Aono, *Sensors*, 2010, **10**, 8604–8634.
- 6 G. Parish, S. Keller, P. Kozodoy, J. Ibbetson, H. Marchand, P. Fini, S. Fleischer, S. DenBaars, U. Mishra and E. Tarsa, *Appl. Phys. Lett.*, 1999, **75**, 247–249.
- 7 K. Liu, D. Shen, C. Shan, J. Zhang, B. Yao, D. Zhao, Y. Lu and X. Fan, *Appl. Phys. Lett.*, 2007, **91**, 201106.
- 8 H. Zhu, C. Shan, B. Yao, B. Li, J. Zhang, D. Zhao, D. Shen and X. Fan, *J. Phys. Chem. C*, 2008, **112**, 20546–20548.
- 9 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, *Adv. Mater.*, 2011, **23**, 649–653.
- 10 P. Shaikh, V. Thakare, D. J. Late and S. Ogale, *Nanoscale*, 2014.
- 11 L. Mandal, N. S. Chaudhari and S. Ogale, *ACS Appl. Mater. Interfaces*, 2013, **5**, 9141–9147.
- 12 L.-H. Zeng, M.-Z. Wang, H. Hu, B. Nie, Y.-Q. Yu, C.-Y. Wu, L. Wang, J.-G. Hu, C. Xie, F.-X. Liang *et al.*, *ACS Appl. Mater. Interfaces*, 2013, **5**, 9362–9366.
- 13 Z. Wang, S. Ran, B. Liu, D. Chen and G. Shen, *Nanoscale*, 2012, **4**, 3350–3358.
- 14 X. Li, C. Gao, H. Duan, B. Lu, X. Pan and E. Xie, *Nano Energy*, 2012, **1**, 640–645.
- 15 Y. Xie, L. Wei, G. Wei, Q. Li, D. Wang, Y. Chen, S. Yan, G. Liu, L. Mei and J. Jiao, *Nanoscale research letters*, 2013, **8**, 1–6.
- 16 S. M. Hatch, J. Briscoe and S. Dunn, *Adv. Mater.*, 2013, **25**, 867–871.
- 17 D. C. Look, *Mater. Sci. Eng., B*, 2001, **80**, 383–387.
- 18 Z. Ju, C. Shan, D. Jiang, J. Zhang, B. Yao, D. Zhao, D. Shen and X. Fan, *Appl. Phys. Lett.*, 2008, **93**, 173505.
- 19 D. Walker, E. Monroy, P. Kung, J. Wu, M. Hamilton, F. Sanchez, J. Diaz and M. Razeghi, *Appl. Phys. Lett.*, 1999, **74**, 762–764.
- 20 D. L. Rogers, *J. Lightwave Technol.*, 1991, **9**, 1635–1638.
- 21 D. Li, X. Sun, H. Song, Z. Li, Y. Chen, H. Jiang and G. Miao, *Adv. Mater.*, 2012, **24**, 845–849.
- 22 S. Han, Z. Zhang, J. Zhang, L. Wang, J. Zheng, H. Zhao, Y. Zhang, M. Jiang, S. Wang, D. Zhao *et al.*, *Appl. Phys. Lett.*, 2011, **99**, 242105.
- 23 M. Liao, Y. Koide and J. Alvarez, *Appl. Phys. Lett.*, 2007, **90**, 123507.
- 24 J. Freouf, T. Jackson, S. Laux and J. Woodall, *Appl. Phys. Lett.*, 1982, **40**, 634–636.
- 25 G. Smit, S. Rogge and T. Klapwijk, *Appl. Phys. Lett.*, 2002, **81**, 3852–3854.
- 26 C. Donolato, *J. Appl. Phys.*, 2004, **95**, 2184–2186.
- 27 V. P. Zhdanov and B. Kasemo, *Physica E*, 2011, **43**, 1486–1489.
- 28 H. Shen, C. Shan, B. Li, B. Xuan and D. Shen, *Appl. Phys. Lett.*, 2013, **103**, 232112.
- 29 G. Tabares, A. Hierro, J. Ulloa, A. Guzman, E. Munoz, A. Nakamura, T. Hayashi and J. Temmyo, *Appl. Phys. Lett.*, 2010, **96**, 101112.
- 30 P.-N. Ni, C.-X. Shan, S.-P. Wang, B.-H. Li, Z.-Z. Zhang, D.-X. Zhao, L. Liu and D.-Z. Shen, *J. Phys. Chem. C*, 2011, **116**, 1350–1353.
- 31 H. Zhu, C. Shan, L. Wang, J. Zheng, J. Zhang, B. Yao and D. Shen, *J. Phys. Chem. C*, 2010, **114**, 7169–7172.
- 32 S. M. Sze, *Semiconductor devices: physics and technology*, John Wiley & Sons, 2008.
- 33 B. Nie, J.-G. Hu, L.-B. Luo, C. Xie, L.-H. Zeng, P. Lv, F.-Z. Li, J.-S. Jie, M. Feng, C.-Y. Wu *et al.*, *Small*, 2013, **9**, 2872–2879.
- 34 J. Liu, C. Shan, B. Li, Z. Zhang, C. Yang, D. Shen and X. Fan, *Appl. Phys. Lett.*, 2010, **97**, 251102.
- 35 X. Xie, Z. Zhang, B. Li, S. Wang, M. Jiang, C. Shan, D. Zhao, H. Chen and D. Shen, *Opt. Express*, 2014, **22**, 246–253.
- 36 Z. Zhang and J. T. Yates Jr, *Chem. Rev.*, 2012, **112**, 5520–5551.
- 37 Z. L. Wang, *Adv. Mater.*, 2012, **24**, 4632–4646.
- 38 O. Katz, V. Garber, B. Meyler, G. Bahir and J. Salzman, *Appl. Phys. Lett.*, 2001, **79**, 1417–1419.
- 39 X. Xie, Z. Zhang, B. Li, S. Wang, M. Jiang, C. Shan, D. Zhao, H. Chen and D. Shen, *Appl. Phys. Lett.*, 2013, **102**, 231122.
- 40 Q. Zheng, F. Huang, K. Ding, J. Huang, D. Chen, Z. Zhan and Z. Lin, *Appl. Phys. Lett.*, 2011, **98**, 221112.

