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Back-to-back asymmetric Schottky-type self-powered UV photodetector based on ternary alloy MgZnO

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Abstract

A back-to-back asymmetric Schottky self-powered UV photodetector (PD) with fast speed was realized by a facile combination of ternary alloy MgZnO film and asymmetric Au electrodes. The high-crystalline-quality MgZnO films were synthesized by metal organic chemical vapor deposition. Due to the incorporation of Mg, the band gap of MgZnO film was confirmed to be 3.76 eV. In addition, owing to the large Schottky barrier difference between the active layer and the two asymmetric Au electrodes, the responsivity of the device could reach up to 2.22 mA W^{-1} at the optical wavelength of 330 nm without any power supply, and with a sharp cutoff at the wavelength of 343 nm. The device exhibits a very low dark current of 247 pA at −5 V. More interestingly, the decay time of our device is only around 92 μs, which is much quicker than any other previously reported UV PDs even with bias voltage applied. Our findings provide a promising approach to realize a high-performance self-powered UV PD.

Keywords: MgZnO, UV PD, self-powered, asymmetric electrodes

(Some figures may appear in colour only in the online journal)

1. Introduction

In the past few decades, self-powered UV photodetectors (PDs) have attracted tremendous attention due to their great potential applications in medical diagnosis, smart communications, health monitoring, materials identification, etc. Human diseases such as cataracts and skin cancers are related to excessive UV radiation in the UVA (320–400 nm) and UVB (280–320 nm) region [1, 2]. Therefore, a smart PD capable of monitoring UV radiation (especially UVA and UVB) without power supply is highly desired to be integrated into the wearable devices for the prevention of excess UV exposure. To date, numerous self-powered UV PDs have been explored. Briefly, they can be divided into two groups according to their ways of energy conversion [3], namely the photoconductive device integrated with an energy harvesting unit, such as the microbial fuel cell, photoelectrochemical cell, piezoelectric resonator, etc [4–7]; and the photovoltaic-based semiconductor p–n homojunction, heterojunction or Schottky junction [8–10]. Although photoconductive devices usually exhibit a high internal gain, the device has a slow response speed and high dark current owing to the conjunction with an additional

power source, the complex energy conversion process and the Ohmic contact electrodes [11, 12]. In contrast, photovoltaic UV PDs can operate by converting UV radiation into electrical signals (e.g. voltage or current) by the built-in electric field. Thus, these types of devices with smaller size usually exhibit a rapid response speed, low dark current and self-powered characteristics. However, the preparation process of the homo or hetero p–n junction device is usually complicated and involves issues such as the reliability of p-doping and lattice mismatch between the film and substrate. Schottky-type UV PDs consisting of metal–semiconductor structure have simpler preparation processes and the advantages of low dark current, high responsivity and fast speed.

Compared with other wide band-gap semiconductors such as TiO_2, ZnO, GaN, AlN and diamond, $Mg_xZn_{1-x}O$ alloy semiconductor has a wide-range band gap (3.37–7.8 eV) tunable by the composition of x. MgZnO also has other advantages in fabricating UV PDs such as being environmentally friendly, biocompatible, and having a low growth temperature (100 °C–750 °C) [13–15]. Although the tough issue of phase separation would take place in $Mg_xZn_{1-x}O$ film, when x is 0.37, the $Mg_xZn_{1-x}O$ alloy still retains wurtzite structure. In addition, the radius of Zn^{2+} and Mg^{2+} is similar. Hence, there were hardly any defects forming during the crystallization process. This means that high-crystal-quality wurtzite structure $Mg_xZn_{1-x}O$ films are excellent candidates for fabricating PDs in the UVA and UVB region. There are many researches in the literature reporting MgZnO UV PDs in metal–semiconductor–metal (MSM) structure. However, the traditional MSM PDs usually require external bias to generate photocurrent due to their two symmetric Schottky contacts connected back-to-back on the planar surface. Self-powered MgZnO-based Schottky-type UV PDs are rarely reported due to the poor electrode contacts in vertical Schottky PDs.

In this work, a novel $Mg_{0.19}Zn_{0.81}O$ self-powered UV PD is constructed with a pair of asymmetric Au metal contacts. Owing to the special back-to-back asymmetric Schottky junctions, photogenerated carries in the active layer can be separated efficiently, very rapidly, without any power supply. The responsivity of the device could reach up to 2.22 mA W^{-1} at the wavelength of 330 nm with a fast speed at 0 V bias. In addition, the device also displays an extremely low dark current of 247 pA at −5 V. This facile and scalable preparation method proposed in this work would provide an additional opportunity to realize high-performance self-powered UV PDs at any other desirable wavelength.

2. Experimental

The sapphire substrate was cleaned with deionized water, acetone and ethyl alcohol, successively. The MgZnO films of about 200 nm were grown on the sapphire substrate using metal organic chemical vapor deposition. Dimethyl dicyclopentadienyl magnesium ($MeCp_2Mg$), diethyl zinc (DEZN) and high-purity (6N) O_2 were used as the precursors. High-purity (6N) nitrogen was used as the carrier gas. The temperature and pressure are kept at 450 °C and 2×10^4 Pa, respectively, during the growth. Au electrodes were deposited by vacuum evaporation. The asymmetric Au interdigital electrodes were patterned using a photolithography process with the widths of 50 and 5 μm (Au electrode #1 and Au electrode #2, respectively) and the separation between the two electrodes is 10 μm). Then, the Au interdigital electrodes were annealed at 500 °C for 60 min.

The morphology and structure of the MgZnO films were characterized by scanning electron microscopy (SEM; Zeiss, Gemini 500), atomic force microscopy (AFM; Bruker, MultiMode-8) and x-ray diffraction (XRD, Bruker, D8 ADVANCE). The response time spectrum was obtained using a pulsed Nd:YAG (266 nm) laser as an excitation source (Continuum, Surelite SL II-10, USA) and an oscilloscope. The room-temperature electrical and photoresponse properties of the fabricated device were measured with a Xe lamp as an excitation source, monochromator and semiconductor characterization system (Agilent B2901A).

3. Result and discussion

The top-view and the cross-sectional SEM images of the MgZnO films grown on the sapphire (0 0 6) substrate are shown in figures 1(a) and (b). Hexagonal grains are observed and the thickness of the films is about 200 nm. The XRD spectrum in figure 1(c) reveals the wurtzite (0 0 2) crystalline orientation of the MgZnO film. The energy-dispersive x-ray (EDS) spectrum (figure 1(d)) shows that the precise molar ratio of Zn:Mg is 0.19:0.81. The AFM image of the MgZnO film obtained by tapping-mode is shown in figure 1(e). As shown in figure 1(f), the optical transmission spectrum of MgZnO films indicates that the films had brilliant transmission performance at visible wavelength, and the band gap is found to be 3.757 eV (see the inset of figure 1(f)). The MgZnO film has a strong absorption at the UVA wavelength. All the images in figure 1 indicate that the crystal quality, surface flatness and optical properties of the MgZnO films have great potential in fabricating UVA PDs.

Figure 2(a) is the schematic figure of this back-to-back asymmetric-type self-powered PD. In order to achieve the self-powered function of the PD, a pair of asymmetric Au interdigital electrodes is fabricated. As shown in the SEM image of figure 2(b), the widths of Au electrode #1 and Au electrode #2 are 50 and 5 μm, respectively, and the separation between them is 10 μm. This asymmetric electrode design is supported by the following explanations. Although the Schottky barrier height of the Au/MgZnO is independent of the contact area between the metal and semiconductor in theory, with the increase of the contact area of the Au/MgZnO Schottky contact, the field intensity of the space-charge region along both the vertical and horizontal directions in the MgZnO films is enhanced. In addition, the number of the accumulated and trapped holes at the two interfaces is different, which induces the difference in the decrease of the Schottky barrier height between electodes#1/MgZnO and electodes#2/MgZnO according to our and other previous works [16–18]. As shown in figure 2(c), in conjunction with dark current and

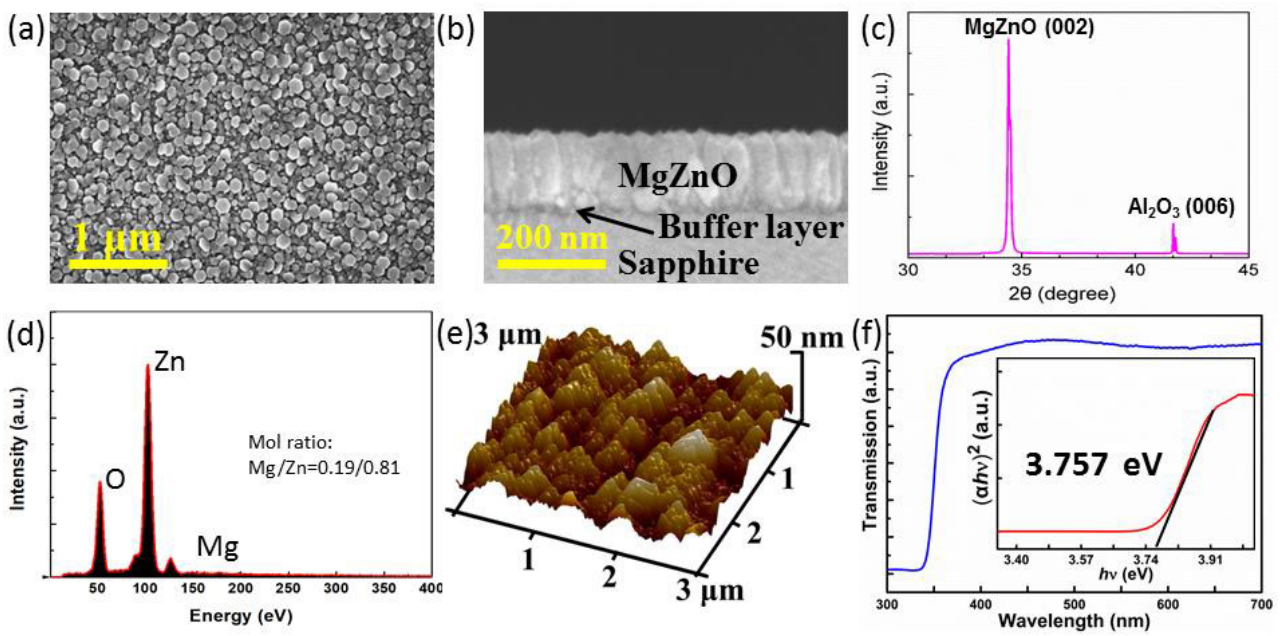

Figure 1. (a) XRD spectrum of the MgZnO films. (b) EDS spectrum of the MgZnO films. (c) Top-view SEM image of the MgZnO films. (d) Cross-section of SEM image of the MgZnO films. (e) 3D image of MgZnO alloy films. (f) Optical transmission spectrum of the MgZnO films at different wavelength. Inset shows the band gap of MgZnO films calculated from the absorption spectrum.

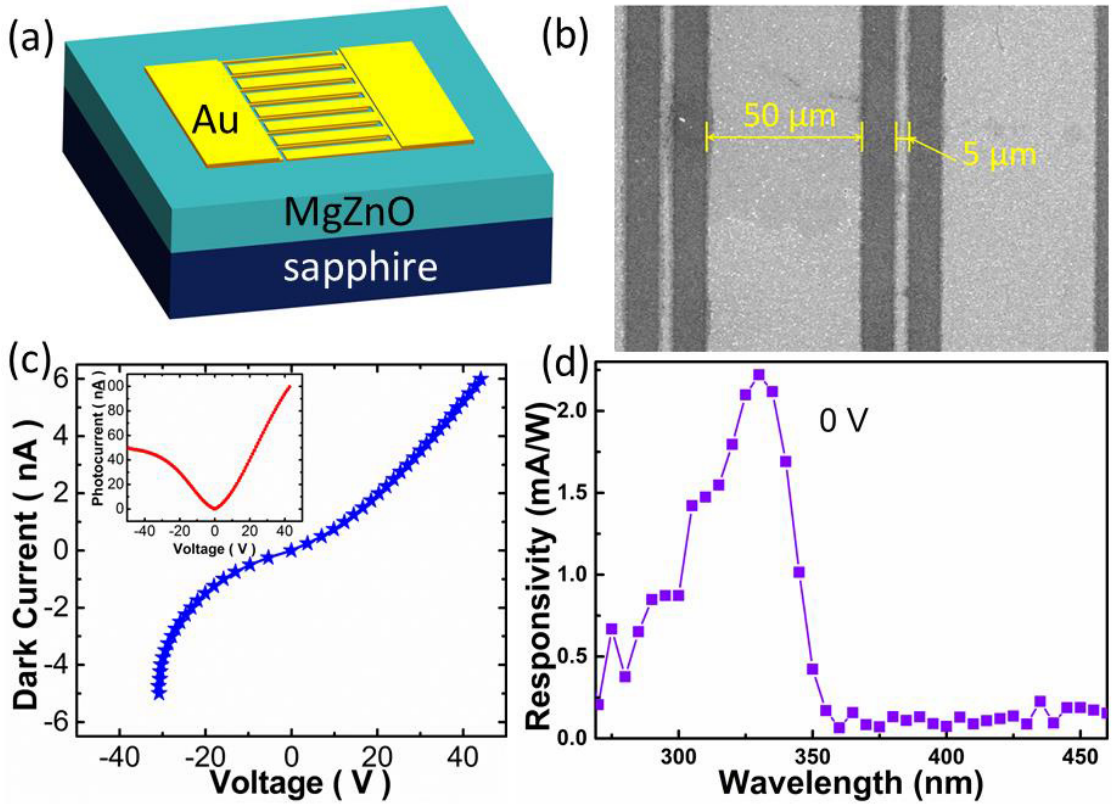

Figure 2. (a) Schematic configuration of the back-to-back asymmetric-type self-powered PD. (b) SEM image of the device. (c) Dark current and photocurrent (inset) at different bias. (d) Responsivity spectra of the device at 0 V bias.

photocurrent (330 nm) of the UVA PD, it was revealed that the asymmetric Schottky contact formed between the Au#1/MgZnO electrodes and Au#2/MgZnO interface.

The UV detection performance of the MgZnO film's PD was precisely examined using a two-probe method under ambient conditions and monochromatic illumination. The responsivity (R) is a vital parameter, and the sensitivity of a PD device is determined by the responsivity, which is defined as the device photocurrent generated per unit power of illumination light, and could be calculated by [19]:

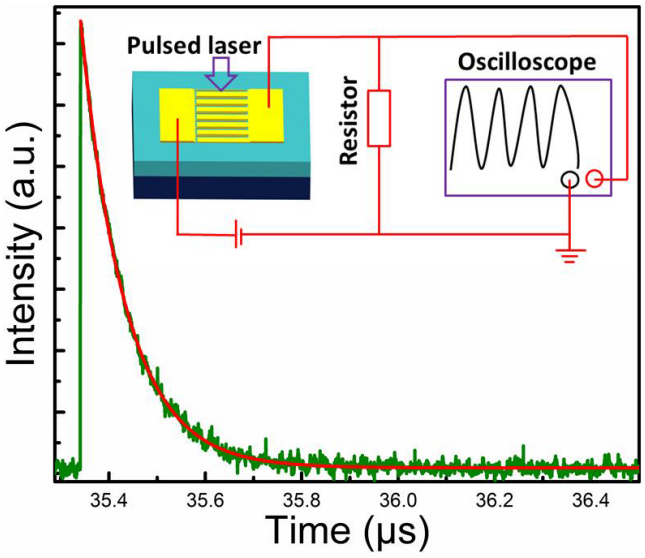

Figure 3. Response time of the device obtained from pulse photoresponse. Inset shows a homemade transient photoresponse measurement system consisting of the pulsed laser and oscilloscope.

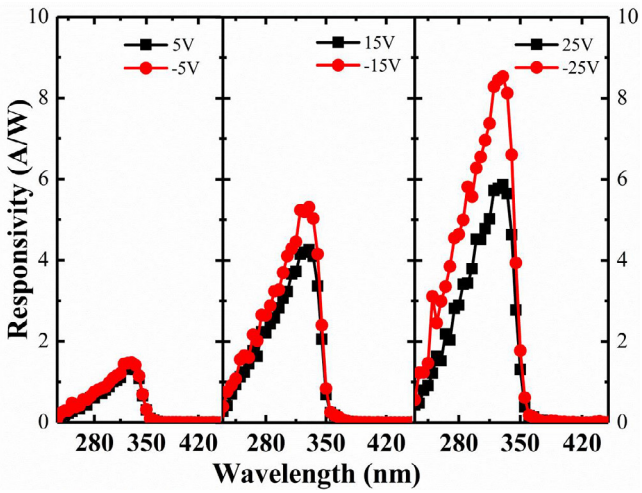

Figure 4. Spectral responsivity of the asymmetric Schottky PD under the bias of 5, 10 and 15 V, respectively.

$$\mathrm{R} = \frac{I_{\mathrm{ph}}}{P}, \tag{1}$$

where I_{ph} is the photocurrent and P is the power of illumination light. In order to obtain the responsivity spectrum of this device, the wavelength selective ability was tested by using a Xe lamp with a monochromator in the range from 280–480 nm at a nominal zero bias. The photocurrent signal was examined when the device was under short-circuit condition during this measurement, to ensure accuracy. As shown in figure 2(d), the PD has an excellent responsivity property under a self-powered mode (0 V bias). The highest responsivity value is 2.22 mA W^{-1}, appearing at 330 nm with a sharp cutoff at 343 nm.

Response time is another key performance parameter for PDs. To test the response time, a homemade transient photoresponse measurement system consisting of a pulsed laser and oscilloscope was set up (shown in figure 3 inset). The loop current increases and results in the increase in partial voltage on the resistor when the PD was illuminated by the pulsed laser (266 nm), and the signal was recorded by the oscilloscope. As shown in figure 3, the photoresponse of this self-powered PD was very fast and highly stable. The decay time was 267 μs, which reveals that this PD is a device having both ultrafast response speed and high photosensitivity.

To further confirm the asymmetric Schottky contact properties of the device, the spectral responsivity of the asymmetric Schottky PD under different bias (5, 15 and 25 V) was measured. As shown in figure 4, it can be seen that the responsivity increases with the bias increasing, and this verifies the fact that the extraction efficiency of photogenerated carriers is proportional to the external bias. Another noteworthy phenomenon is that the responsivity under backward voltages was larger than those under forward voltages as the external bias increased. This is due to the asymmetry of the Au electrodes. Although this back-to-back asymmetric Au/MgZnO Schottky type PD works at 0 V bias, better performance is achieved with the increase of bias. Detectivity (D^*) is a crucial parameter of PD reflecting the ability of weak signal detection, and is given by:

$$D^* = \frac{R}{(2qI_{\mathrm{d}}/S)^{\frac{1}{2}}}\ \text{(Jones)}, \tag{2}$$

where R is the photoresponsivity, q is the unit charge, and I_{d} and S are, respectively, the dark current and effective irradiated area. Due to the excellent photoresponsivity and exceedingly small dark current, the D^* of this PD is 4.4×10^{11} Jones at 5 V bias. Therefore, this asymmetric Schottky UV PD has brilliant performance on weak signal. In addition, the comparison between the device in this study and other reported self-powered UV PDs is listed in table 1. It can be found that the comprehensive performance of our PD is much higher than that of the other present self-powered UV PDs.

Energy-band theory could explain clearly the effects on the asymmetric electrodes while the external bias of the PD device is at 0 V. The energy-band diagrams of the asymmetric electrodes' PD under 0 V bias are shown in figure 5. In the dark condition, as shown in figure 5(a), the same Schottky barrier heights were formed between the MgZnO films' interface and Au electrodes #1 and #2. The Au electrodes and MgZnO films had the same Femi level (E_{F}). The electrode having the larger contact area corresponded to a wider depletion region formed at the interface. Hence, the width of the depletion region at Au electrode #1 should be larger than that of Au electrode #2 [25–27]. Figure 5(b) indicated that electron–hole is generated in the MgZnO films under UV illumination, the photogenerated electrons in the conduction band move away from contact, and the photogenerated holes in the valence band move towards the contact. The drifted electrons and holes at the interfaces changed the original electric potential profile and resulted in the lowering of the Schottky barriers [28–30]. The asymmetric electrodes having different electric potential profile and depletion widths thus induced different carrier separation and transport. As a result, the two electrodes collected different numbers of trapped holes that formed different heights of the Schottky barriers at the two asymmetric

Table 1. Comparison of the characteristic parameters of other self-powered UV PDs.

Materials	Wavelength (nm)	Dark current (A)	Rise/decay time (s)	Responsivity at 0 V bias (A W^{-1})	D^* (Jones)	Ref.
Au–TiO_2–Au	365	1.5×10^{-5}	0.08/0.03	6.06	—	[11]
n-ZnO/p-Cu_2O	375	8.5×10^{-5}	0.36/0.14	8.2×10^{-3}	—	[20]
n-ZnO/p-NiO	355	4.5×10^{-7}	0.23/0.21	4.4×10^{-4}	—	[21]
n-ZnO/p-GaN	325	1.3×10^{-9}	2×10^{-5}/2.19×10^{-4}	1.81	—	[22]
Diamond/Ga_2O_3	244	5.5×10^{-8}	—/—	2×10^{-4}	6.9×10^{9}	[23]
Cr/Au–Zn_2GeO_4–Cr/Au	260	—	1×10^{-2}/1.3×10^{-2}	5.11×10^{-3}	2.91×10^{11}	[24]
Au#1–MgZnO–Au#2	330	2.47×10^{-7}	2.3×10^{-7}/9.2×10^{-5}	2.22×10^{-3}	4.4×10^{11}	This work

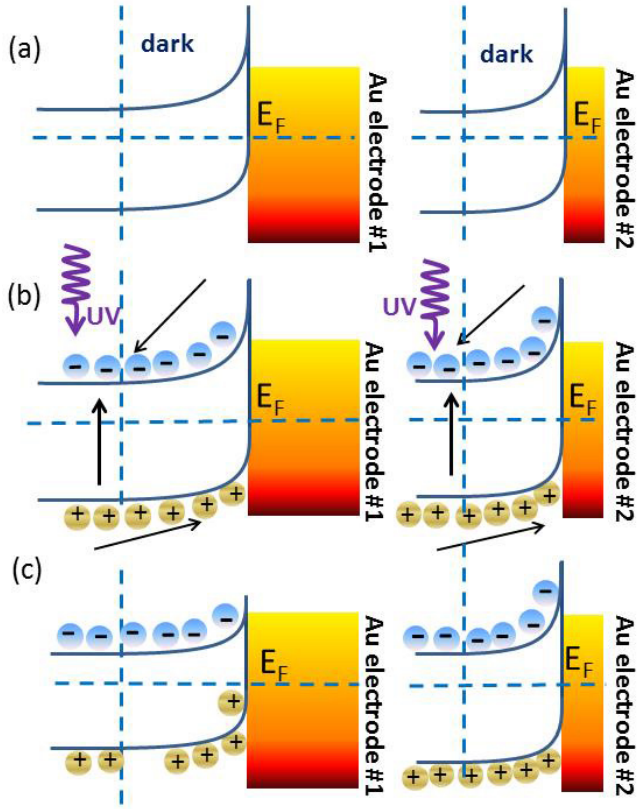

Figure 5. Energy-band diagrams of the asymmetric electrodes' PD at 0 V, (a) in the dark, (b) and (c) under UV light.

electrodes. In the end, the self-powered function of PDs could be achieved by this simple electrode design.

4. Conclusions

In summary, a novel self-powered PD was proposed based on the hexagonal MgZnO alloy films. Owing to the specially designed asymmetric Au planar electrodes on the active layer, the device exhibited excellent photovoltaic properties in the UV region. The responsivity of the device could reach up to 2.22 mA W^{-1} at the wavelength of 330 nm without any power supply and with a sharp cutoff at 343 nm. In addition, the device exhibited a very low dark current of 247 pA at −5 V. The origin of the photoresponse at 0 V in our devices should be associated with the asymmetric accumulated and trapped holes at the Au/MgZnO interfaces. Our findings in this work would provide a facile route to realize high-performance self-powered UV PDs based on the alloy semiconductors at any other desired wavelength.

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References

[1] Chao J, Wang Z, Xu X, Xiang Q, Song W, Chen G, Hu J and Chen D 2013 Tin sulfide nanoribbons as high performance photoelectrochemical cells, flexible photodetectors and visible-light-driven photocatalysts *RSC Adv.* **3** 2746–53
[2] Chen H, Liu K, Hu L, Al-Ghamdi A A and Fang X 2015 New concept ultraviolet photodetectors *Mater. Today* **18** 493–502
[3] Chen H, Yu P, Zhang Z, Teng F, Zheng L, Hu K and Fang X 2016 Ultrasensitive self-powered solar-blind deep-ultraviolet photodetector based on all-solid-state polyaniline/MgZnO bilayer *Small* **12** 5809–16
[4] Donolato C 2004 Approximate analytical solution to the space charge problem in nanosized Schottky diodes *J. Appl. Phys.* **95** 2184–6
[5] Feng Y, Zhang Y, Wang Y and Wang Z 2018 Frequency response characteristics of pyroelectric effect in p–n junction UV detectors *Nano Energy* **54** 429–36
[6] Freeouf J L, Jackson T N, Laux S E and Woodall J M 1982 Effective barrier heights of mixed phase contacts: size effects *Appl. Phys. Lett.* **40** 634–6

[7] Goykhman I, Sassi U, Desiatov B, Mazurski N, Milana S, de Fazio D, Eiden A, Khurgin J, Shappir J and Levy U 2016 On-chip integrated, silicon–graphene plasmonic Schottky photodetector with high responsivity and avalanche photogain *Nano Lett.* **16** 3005–13
[8] Guo D, Su Y, Shi H, Li P, Zhao N, Ye J, Wang S, Liu A, Chen Z and Li C 2018 Self-powered ultraviolet photodetector with superhigh photoresponsivity (3.05 A W^{-1}) based on the GaN/Sn: Ga2O3 p–n junction *ACS Nano* **12** 12827–35
[9] Hu L, Yan J, Liao M, Xiang H, Gong X, Zhang L and Fang X 2012 An optimized ultraviolet-A light photodetector with wide-range photoresponse based on ZnS/ZnO biaxial nanobelt *Adv. Mater.* **24** 2305–9
[10] Katz O, Garber V, Meyler B, Bahir G and Salzman J 2001 Gain mechanism in GaN Schottky ultraviolet detectors *Appl. Phys. Lett.* **79** 1417–9
[11] Li X, Gao C, Duan H, Lu B, Pan X and Xie E 2012 Nanocrystalline TiO_2 film based photoelectrochemical cell as self-powered UV-photodetector *Nano Energy* **1** 640–5
[12] Matsumura Y and Ananthaswamy H N 2004 Toxic effects of ultraviolet radiation on the skin *Toxicol. Appl. Pharmacol.* **195** 298–308
[13] Smit G D J, Rogge S and Klapwijk T M 2002 Scaling of nano-Schottky-diodes *Appl. Phys. Lett.* **81** 3852–4
[14] Wang C, Chang S-J, Su Y-K, Chiou Y-Z, Chen S, Chang C, Lin T, Liu H and Tang J-J 2005 GaN MSM UV photodetectors with titanium tungsten transparent electrodes *IEEE Trans. Electron Devices* **53** 38–42
[15] Wang Z L 2012 Progress in piezotronics and piezo-phototronics *Adv. Mater.* **24** 4632–46
[16] Chen H Y, Liu K W, Chen X, Zhang Z Z, Fan M M, Jiang M M, Xie X H, Zhao H F and Shen D Z 2014 Realization of a self-powered ZnO MSM UV photodetector with high responsivity using an asymmetric pair of Au electrodes *J. Mater. Chem.* C **2** 9689–94
[17] Su L, Chen H Y, Xu X and Fang X S 2017 Novel BeZnO based self-powered dual-color UV photodetector realized via a one-step fabrication method *Laser Photonics Rev.* **11** 1700222
[18] Xu J, Yang W, Chen H Y, Zheng L, Hu M, Li Y and Fang X S 2018 Efficiency enhancement of TiO_2 self-powered UV photodetectors using a transparent Ag nanowire electrode *J. Mater. Chem.* C **6** 3334–40
[19] Xie F, Lu H, Xiu X, Chen D, Han P, Zhang R and Zheng Y 2011 Low dark current and internal gain mechanism of GaN MSM photodetectors fabricated on bulk GaN substrate *Solid State Electron.* **57** 39–42
[20] Bai Z and Zhang Y 2016 Self-powered UV–visible photodetectors based on ZnO/Cu_2O nanowire/electrolyte heterojunctions *J. Alloys Compd.* **675** 325–30
[21] Shen Y, Yan X, Bai Z, Zheng X, Sun Y, Liu Y, Lin P, Chen X and Zhang Y 2015 *RSC Adv.* **5** 5976–81
[22] Bie Y, Liao Z, Zhang H, Li G, Ye Y, Zhou Y, Xu J, Qin Z, Dai L and Yu D P 2011 Self-powered, ultrafast, visible-blind UV detection and optical logical operation based on ZnO/GaN nanoscale p-n junctions *Adv. Mater.* **23** 649–53
[23] Chen Y C, Lu Y J, Lin C N, Tian Y Z, Gao C J, Dong L and Shan C X 2018 Self-powered diamond/β-Ga_2O_3 photodetectors for solar-blind imaging *J. Mater. Chem.* C **6** 5727–32
[24] Zhou X, Zhang Q, Gan L, Li X, Li H, Zhang Y, Golberg D and Zhai T 2016 High-performance solar-blind deep ultraviolet photodetector based on individual single-crystalline Zn_2GeO_4 nanowire *Adv. Funct. Mater.* **26** 704–12
[25] Xie X, Zhang Z, Li B, Wang S, Jiang M, Shan C, Zhao D, Chen H and Shen D 2014 Enhanced solar-blind responsivity of photodetectors based on cubic MgZnO films via gallium doping *Opt. Express* **22** 246–53
[26] Xie X H, Zhang Z Z, Li B H, Wang S P and Shen D Z 2013 Mott-type $Mg_xZn_{1-x}O$-based visible-blind ultraviolet photodetectors with active anti-reflection layer *Appl. Phys. Lett.* **102** 231122
[27] Xu X, Chen J, Cai S, Long Z, Zhang Y, Su L, He S, Tang C, Liu P and Peng H 2018 A real-time wearable UV-radiation monitor based on a high-performance p-CuZnS/n-TiO_2 photodetector *Adv. Mater.* **30** 1803165
[28] Yang Q, Guo X, Wang W, Zhang Y, Xu S, Lien D H and Wang Z L 2010 Enhancing sensitivity of a single ZnO micro-/nanowire photodetector by piezo-phototronic effect *ACS Nano* **4** 6285–91
[29] Zhang F, Ding Y, Zhang Y, Zhang X and Wang Z L 2012 Piezo-phototronic effect enhanced visible and ultraviolet photodetection using a ZnO–CdS core–shell micro/nanowire *ACS Nano* **6** 9229–36
[30] Zhu H, Shan C, Wang L, Zheng J, Zhang J, Yao B and Shen D 2010 Metal-oxide- semiconductor-structured MgZnO ultraviolet photodetector with high internal gain *J. Phys. Chem.* C **114** 7169–72