

Self-Powered Ultraviolet Photodetector with Superhigh Photoresponsivity (3.05 A/W) Based on the GaN/Sn:Ga₂O₃ pn Junction

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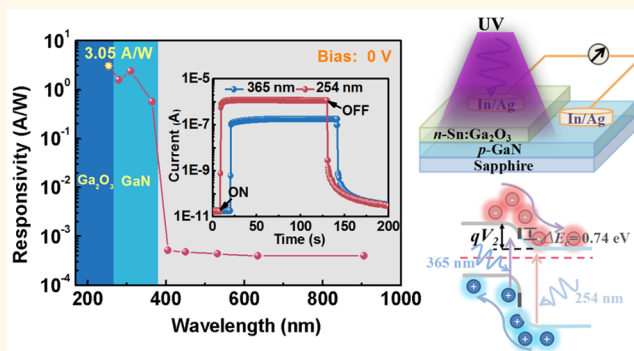
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ABSTRACT: Ultraviolet (UV) radiation has a variety of impacts including the health of humans, the production of crops, and the lifetime of buildings. Based on the photovoltaic effect, self-powered UV photodetectors can measure and monitor UV radiation without any power consumption. However, the current low photoelectric performance of these detectors has hindered their practical use. In our study, a super-high-performance self-powered UV photodetector based on a GaN/Sn:Ga₂O₃ pn junction was generated by depositing a Sn-doped n-type Ga₂O₃ thin film onto a p-type GaN thick film. The responsivity at 254 nm reached up to 3.05 A/W without a power supply and had a high UV/visible rejection ratio of $R_{254\text{ nm}}/R_{400\text{ nm}} = 5.9 \times 10^3$ and an ideal detectivity at $1.69 \times 10^{13} \text{ cm}^2 \cdot \text{Hz}^{1/2} \cdot \text{W}^{-1}$, which is well beyond the level of previous self-powered UV photodetectors. Moreover, our device also has a low dark current ($1.8 \times 10^{-11} \text{ A}$), a high $I_{\text{photo}}/I_{\text{dark}}$ ratio ($\sim 10^4$), and a fast photoresponse time of 18 ms without bias. These outstanding performance results are attributed to the rapid separation of photogenerated electron–hole pairs driven by a high built-in electric field in the interface depletion region of the GaN/Sn:Ga₂O₃ pn junction. Our results provide an improved and easy route to constructing high-performance self-powered UV photodetectors that can potentially replace traditional high-energy-consuming UV detection systems.

KEYWORDS: self-powered, ultraviolet photodetector, GaN/Sn:Ga₂O₃ pn junction, superhigh photoresponsivity, 3.05 A/W, potential barrier



Ultraviolet radiation has a significant impact on humankind. Some benefits are UV's ability to facilitate the synthesis of vitamin D, kill germs, and treat or prevent rickets when our skin is exposed to moderate UV light.¹ However, it can cause cataracts and skin cancer and accelerate the aging process due to an excessive amount of UV radiation.^{1,2} Additionally, UV radiation strongly affects the production of crops and the lifetime of buildings. Fortunately, UV radiation can be measured and monitored using semiconductor UV photodetectors based on Einstein's photoelectric effect, which transforms UV radiation to measurable electronic signals. After decades of steady development, modern UV photodetectors, with high performances in photoresponsivity, signal-to-noise ratios, stability, and speed, have gained interest recently for their applications in

environmental monitoring, advanced communications, air purification, leak detection, space research, etc.^{3–13}

Unfortunately, to acquire reasonable detectivity, an external electric field is applied to photodetectors to separate the photogenerated electron–hole pairs.^{5–13} Therefore, external power sources are generally necessary. This makes photodetectors overall uneconomical and complex. On the contrary, self-powered photodetectors can help solve the energy issues and have attracted significant attention.^{14–19} Compared to traditional photodetectors, self-powered structures, based on the photovoltaic effect such as pn junctions, heterojunctions,

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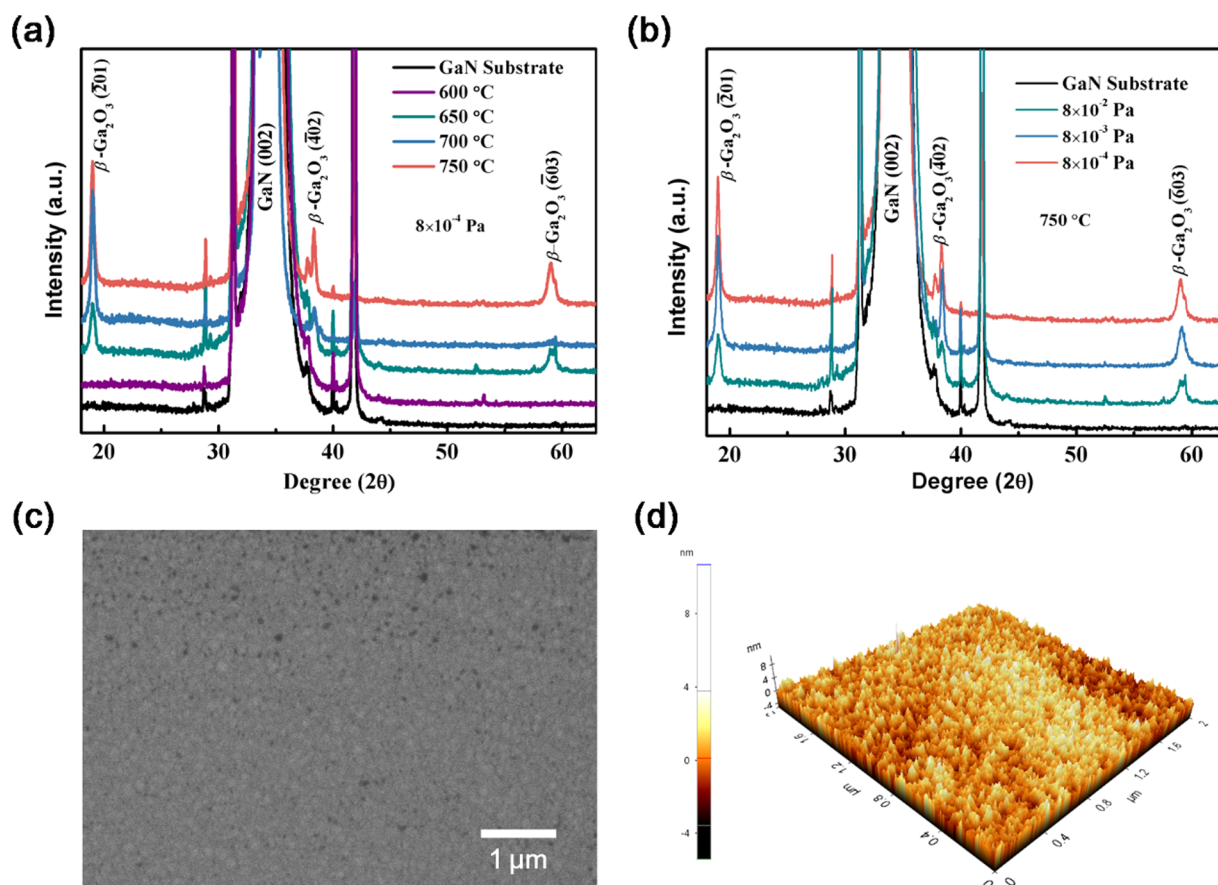


Figure 1. XRD patterns of Sn:Ga₂O₃ thin films deposited on a GaN film substrate at different (a) substrate temperatures and (b) oxygen pressures. (c) FE-SEM plane-view and (d) AFM images of the surface morphology for Sn:Ga₂O₃ thin films deposited on a GaN film at 8 × 10⁻⁴ Pa and 750 °C.

Schottky junctions, and organic/inorganic hybrid junctions, separate the electron–hole pairs rapidly with the built-in electric field.²⁰ This reveals a higher photosensitivity and faster photoresponse at zero bias without consuming external power.^{14–21} Self-powered UV photodetectors have great application potential. They not only are used to detect humidity and toxic gas sensitivity but also function as batteries or hybrid supercapacitors.¹

For self-powered UV photodetectors, the photoresponsivities are still low for practical applications even though great progress has been made in recent years.¹ Shen *et al.* fabricated self-powered UV photodetectors using an n-ZnO/p-NiO core–shell nanowire array heterojunction and a Au/β-Ga₂O₃ nanowire array film Schottky junction with responsivities of 0.49 and 0.01 mA/W, respectively.^{14,21} Fang *et al.* prepared a highly crystalline individual ZnO–Ga₂O₃ core–shell heterojunction, which shows a responsivity of 9.7 mA/W at 251 nm under zero bias.¹⁵ Zheng *et al.* first constructed a back-to-back p-graphene/AlN/p-GaN vacuum ultraviolet photovoltaic detector, which exhibits a responsivity of 67 mA/W and an extremely fast response of 80 ns at 0 V.¹¹ In previous work, our group constructed a heterojunction based on Ga₂O₃/NSTO,²² Ga₂O₃/GaZnO,¹⁷ and p-GaN/n-Ga₂O₃²³ for self-powered UV photodetectors, which exhibits responsivities of 2.6 mA/W (254 nm), 0.763 mA/W (254 nm), and 54.43 mA/W (365 nm), respectively. Among these photodetectors, the pn junction based on the GaN/Ga₂O₃ heterojunction with a suitable energy band potential barrier led to innovation for the

next generation of self-powered UV photodetectors. The p-type GaN thin film layer can be obtained easily by doping Mg.^{24,25} β-Ga₂O₃ shows an intrinsic n-type semiconductor due to oxygen deficiency.^{26–29} To engineer high-performance GaN/Ga₂O₃-based self-powered UV photodetectors, it is crucial to understand the physical mechanisms. The photo-generated carriers need to be separated by the built-in potential between GaN and Ga₂O₃; therefore an energy band structure with a large built-in electric field is essential. In our previous paper, we used the intrinsic Ga₂O₃ acting as n-type.²³ If β-Ga₂O₃ is doped with tetravalent elements, the Fermi level will move close to the conduction band. As a result, the built-in potential barrier will be larger and the separation of the photogenerated carriers will be more effective and fast. Herein, the pn junctions based on GaN/Sn-doped Ga₂O₃ (GaN/Sn:Ga₂O₃) are constructed by depositing Sn:Ga₂O₃ thin films on p-type GaN films. The GaN/Sn:Ga₂O₃ junction shows a superhigh photoresponsivity of 3.05 A/W under 254 nm UV light and under zero bias. This exhibits applications for communication and space detection.

RESULTS AND DISCUSSION

The p-type Mg:GaN thin films have a band gap of 3.38 eV and are sensitive to UV light at wavelengths less than 367 nm.²³ Various substrate temperatures and oxygen pressures were explored to grow a Sn:Ga₂O₃ thin film. The X-ray diffraction (XRD) patterns of GaN/Sn:Ga₂O₃ pn junctions prepared at different growth conditions are shown in Figure 1(a) and (b).

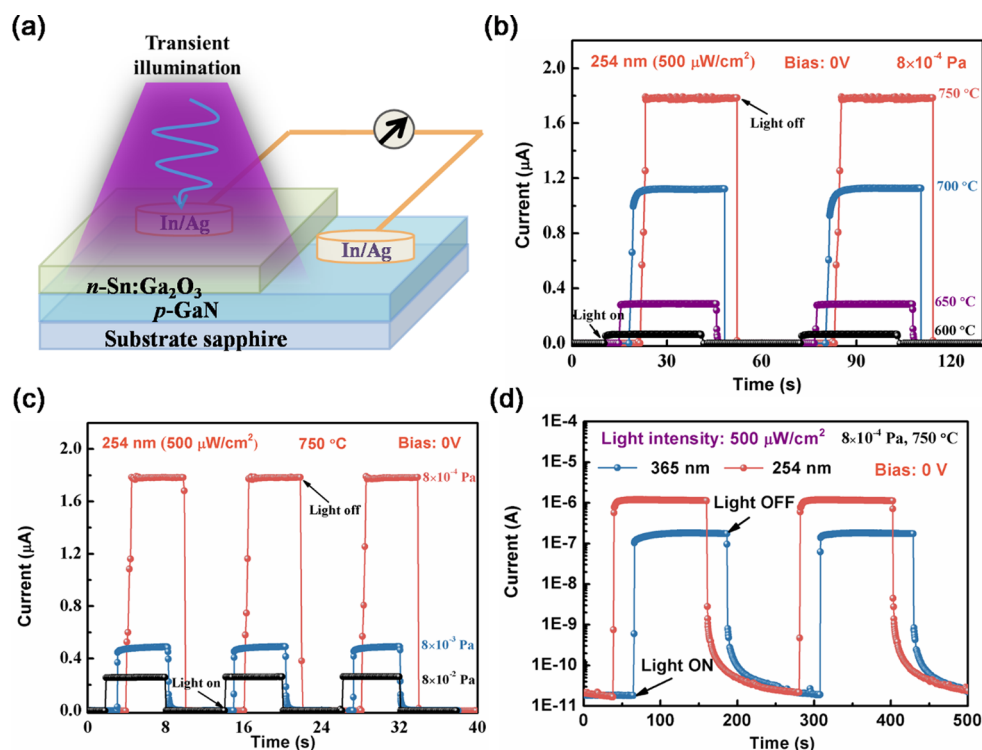


Figure 2. (a) Schematic illustration of the fabricated prototype GaN/Sn:Ga₂O₃ pn junction photodetector; time-dependent photoresponse of the GaN/Sn:Ga₂O₃ pn junction photodetector with the Sn:Ga₂O₃ thin films grown under different (b) substrate temperatures and (c) oxygen pressures by periodically turning on and off the 254 nm UV illumination (with a light intensity of 500 μW/cm²) at zero bias. (d) Time-dependent photoresponse of the GaN/Sn:Ga₂O₃ pn junction photodetector with the Sn:Ga₂O₃ thin films grown at 8 × 10⁻⁴ Pa and 750 °C by periodically turning on and off the 365 and 254 nm UV illumination with a light intensity of 500 μW/cm² at zero bias.

No peaks relating to Ga₂O₃ were observed in the XRD pattern of the film deposited at 600 °C. There were, however, peaks corresponding to the substrate. As shown in Figure 1(a), the XRD pattern exhibited an amorphous structure, possibly due to the lack of kinetic energy for the formation of β-Ga₂O₃ films.²⁷ At a substrate temperature of 650 °C, the thin film starts to crystallize with the presence of three peaks located at 18.83°, 38.17°, and 58.86°, respectively, which corresponds to the (201) and higher order diffraction lattice plane of β-Ga₂O₃.³⁰ The crystallization quality of β-Ga₂O₃ thin films improves as the substrate temperature increases up to 750 °C under the fixed oxygen pressure of 8 × 10⁻⁴ Pa [Figure 1(a)]. With an increase of oxygen pressure, the peak intensities of (201) and higher order diffraction lattice planes from Ga₂O₃ decrease at the substrate temperature of 750 °C [Figure 1(b)]. Comparing the growth conditions above, the thin films prepared at 8 × 10⁻⁴ Pa and 750 °C have a better crystallization with an out-of-plane relationship of β-Ga₂O₃ (201) parallel to GaN (002). Figure 1(c) shows the plane-view image of the Sn:Ga₂O₃ thin films deposited on a Mg:GaN film substrate at a pressure of 8 × 10⁻⁴ Pa and a temperature of 750 °C using a field emission scanning electron microscope (FE-SEM). Figure 1(d) shows the surface morphology of the thin film obtained using an atomic force microscope (AFM) with a scanning area of 2 × 2 μm. The root-mean-square (RMS) surface roughness obtained is 4.76 nm.

The contacts between the In/Ag electrodes and GaN or Ga₂O₃ thin films are ohmic and have been investigated and given in our previous work.²³ Figure 2(a) displays a schematic illustration of the fabricated prototype heterojunction photodetector. The UV photoelectric properties of GaN/Sn:Ga₂O₃

pn junctions prepared under various substrate temperatures and oxygen pressures are measured. Figure 2(b) and (c) show the time-dependent photoresponse by intermittently turning on and off the 254 nm UV illumination with an intensity of 500 μW/cm² under an applied bias of 0 V. The photocurrent increases as the substrate temperature increases from 600 °C up to 750 °C under a fixed oxygen pressure of 8 × 10⁻⁴ Pa. However, the photocurrent decreases as the oxygen pressure increases at a fixed substrate temperature of 750 °C. As a result, the GaN/Sn:Ga₂O₃ pn junction photodetector with the Sn:Ga₂O₃ thin films grown under an oxygen pressure of 8 × 10⁻⁴ Pa and a substrate temperature of 750 °C exhibits the best photocurrent. All of the following investigations are performed based on the above growth conditions.

Figure 2(d) shows the time-dependent photoresponse by intermittently switching on and off the 365 and 254 nm UV illumination. The intensities for both UV radiations are 500 μW/cm² under zero bias. The dark current is approximately 1.8 × 10⁻¹¹ A. When the 365 nm UV light was turned on, the current detected increases instantly to 1.7 × 10⁻⁷ A, with the ratio of $I_{\text{photo}}/I_{\text{dark}}$ being approximately 4 orders of magnitude ($\sim 10^4$), exhibiting the characteristic of being self-powered. When the UV light is turned off, the current drops to the dark count. For the 254 nm UV light, the $I_{\text{photo}}/I_{\text{dark}}$ ratio of the GaN/Sn:Ga₂O₃ pn junction photodetector is about 6.1 × 10⁴ with a photocurrent of 1.1 × 10⁻⁶ A.

These results show that the photodetector based on GaN/Sn:Ga₂O₃ pn junction functions without an external power supply. The zero power consumption observed is attributed to the photovoltaic properties of the pn junction between GaN and Sn:Ga₂O₃, as shown in Figure 3. The *I*–*V* curve of the

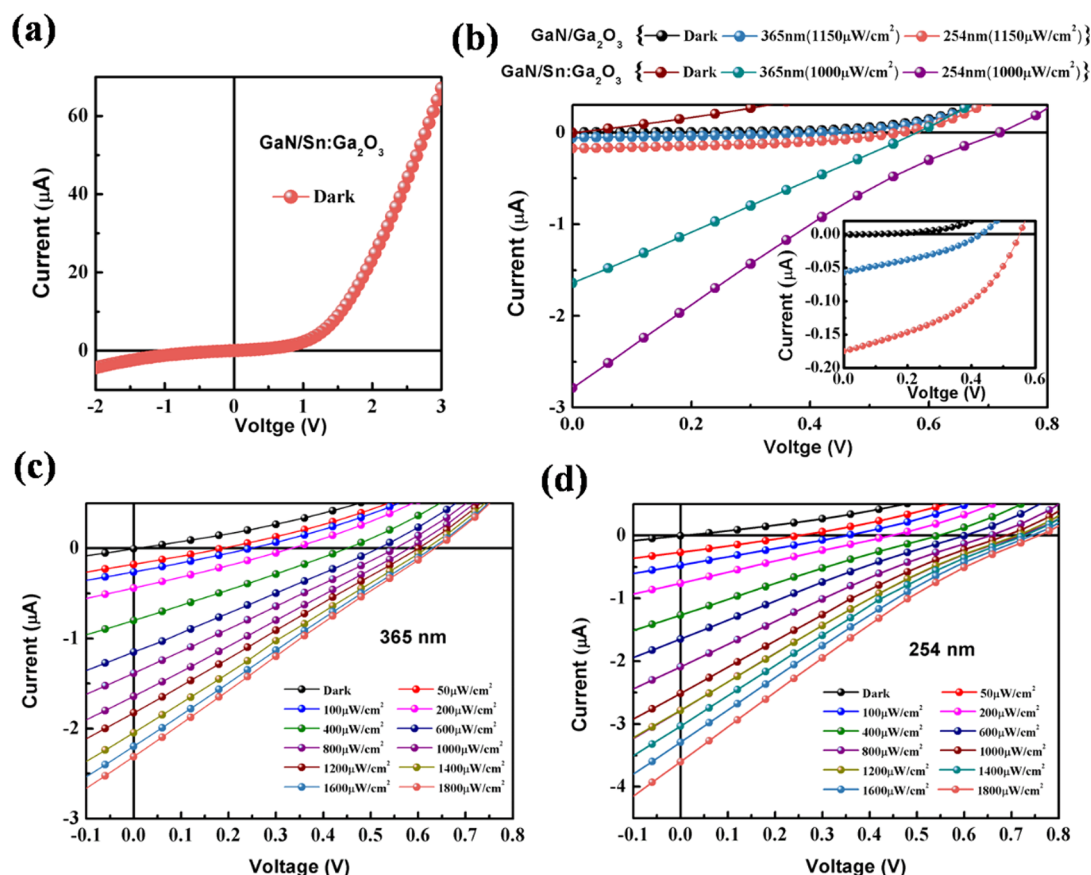


Figure 3. (a) *I*–*V* characteristic curve of the GaN/Sn:Ga₂O₃ pn junction photodetector in the dark; (b) Comparison of the *I*–*V* enlarged curves near zero bias between the GaN/Ga₂O₃ pn junction photodetector and the Sn doping GaN/Sn:Ga₂O₃ pn junction photodetector in the dark, at 365 and 254 nm illumination; *I*–*V* curves of the GaN/Sn:Ga₂O₃ pn junction photodetector with the Sn:Ga₂O₃ thin films grown at 8×10^{-4} Pa and 750 °C in the dark at (c) 365 nm and (d) 254 nm illumination with various light intensities.

GaN/Sn:Ga₂O₃ pn junction presents typical rectifying characteristics (Figure 3(a)), which is similar to that of the GaN/Ga₂O₃ pn junction, indicating that the GaN/Sn:Ga₂O₃ junction functions as a well-defined diode. In solar cells, when the negative photocurrent under voltage reaches zero, it is called a short-circuit current, which is due to the generation and collection of light-generated carriers. The short-circuit current is an important parameter for solar cells. Compared to the GaN/Ga₂O₃ junction, the Sn doping GaN/Sn:Ga₂O₃ pn junction photodetector exhibits a large enhanced short-circuit current, which is depicted in Figure 3(b). When the intensity of the illumination reaches 1150 μW/cm², the short-circuit current of the GaN/Ga₂O₃ pn junction photodetector is 0.175 and 0.058 μA at 365 and 254 nm UV illuminations, respectively (inset panel of Figure 3(b)). When the intensity of the illumination is 1000 μW/cm², the short-circuit currents of the GaN/Sn:Ga₂O₃ pn junction photodetector are 1.641 and 2.785 μA at 365 and 254 nm illuminations, respectively. When the thin film is illuminated with 254 nm UV light, the short-circuit current is enhanced 48 times for the Sn-doped Ga₂O₃ thin film. One advantage of this device is that it does not need an external power source; the photodetector generates a nonequilibrium carrier through radiation. Figure 3(c) and (d) show the enlarged current (*I*) versus voltage (*V*) properties of the GaN/Sn:Ga₂O₃ pn junction photodetector at 365 and 254 nm UV light under various light intensities, respectively, at zero bias. In the dark, the *I*–*V* curve passes through the origin of the coordinate. When the photodetector

is exposed to 254 or 365 nm UV light, the *I*–*V* curve deviates from the coordinate origin and exhibits a negative photocurrent under zero bias. Under the illumination of a fixed light intensity, the short-circuit current increases concomitantly with increased intensity of illumination. At a light intensity of 1800 μW/cm², the short-circuit current values are 2.3 and 3.6 μA at 365 and 254 nm UV light, respectively. The intensity of the radiation is detected by measuring the photoelectric voltage or current. The results from above show that a GaN/Sn:Ga₂O₃ pn junction photodetector can function without an external power source, making it therefore a self-powered device, which has potentially important applications such as secure ultraviolet communication and space detection.

As shown in Figure 4(a), the continuous time-dependent photoresponse cycles of the photodetector have a nearly identical response under 254 nm light and 365 nm light illumination with a light intensity of 1000 μW/cm² and at zero bias, showing high robustness and good reproducibility. A measurement under 254 nm UV light illumination with an intensity ranging from 50 to 1800 μW/cm² was used to evaluate the influence of intensity on the response of the photodetector (Figure 4(b)). Figure 4(c) shows the photocurrent and responsivity of the photodetector as a function of the intensity of illuminating light. The photocurrent increases almost linearly as the intensity of the illumination increases. A higher light intensity would produce more photogenerated electron–hole pairs, resulting in a higher photocurrent. Responsivity (*R*), a photodetector parameter to evaluate

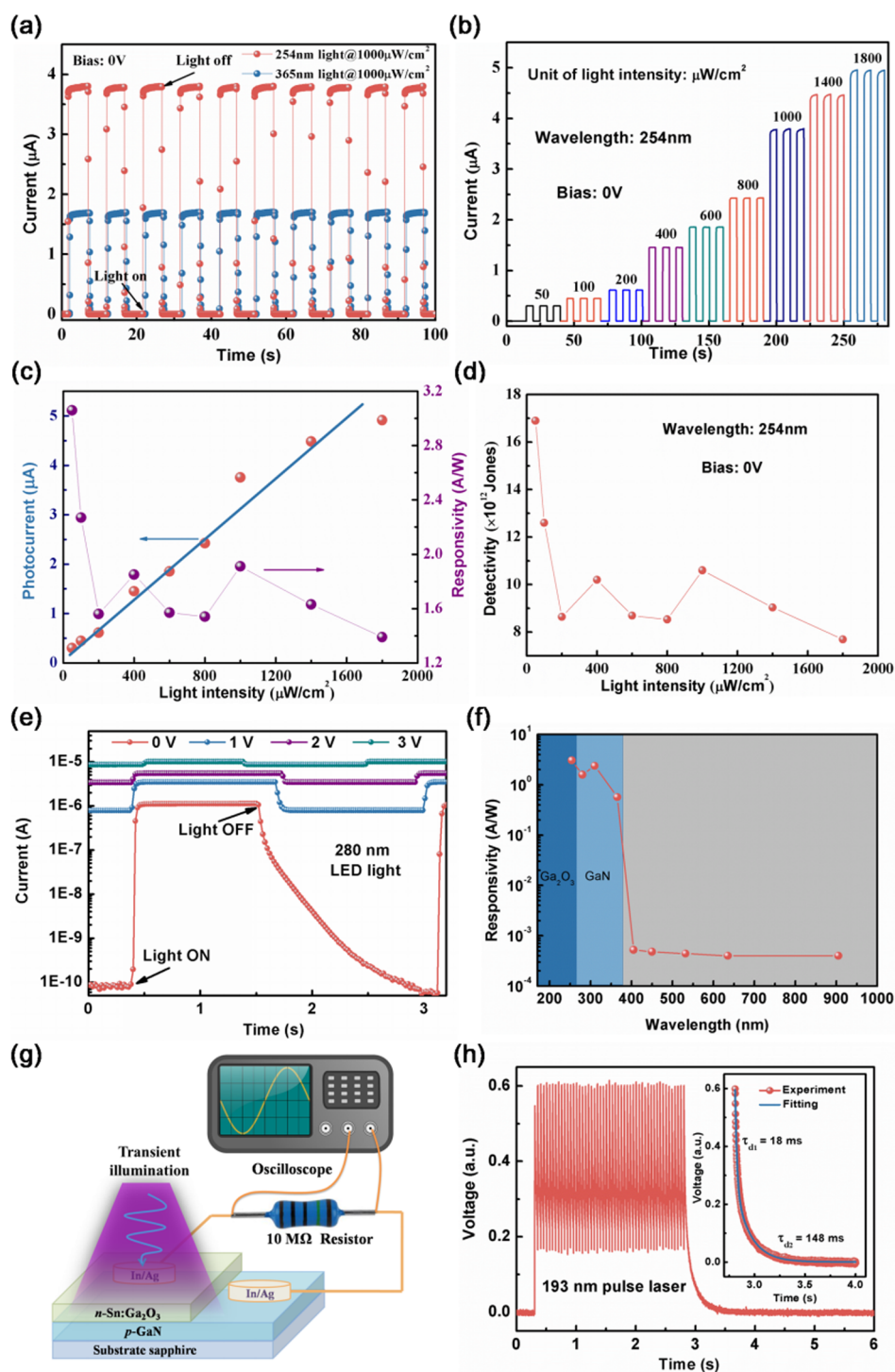


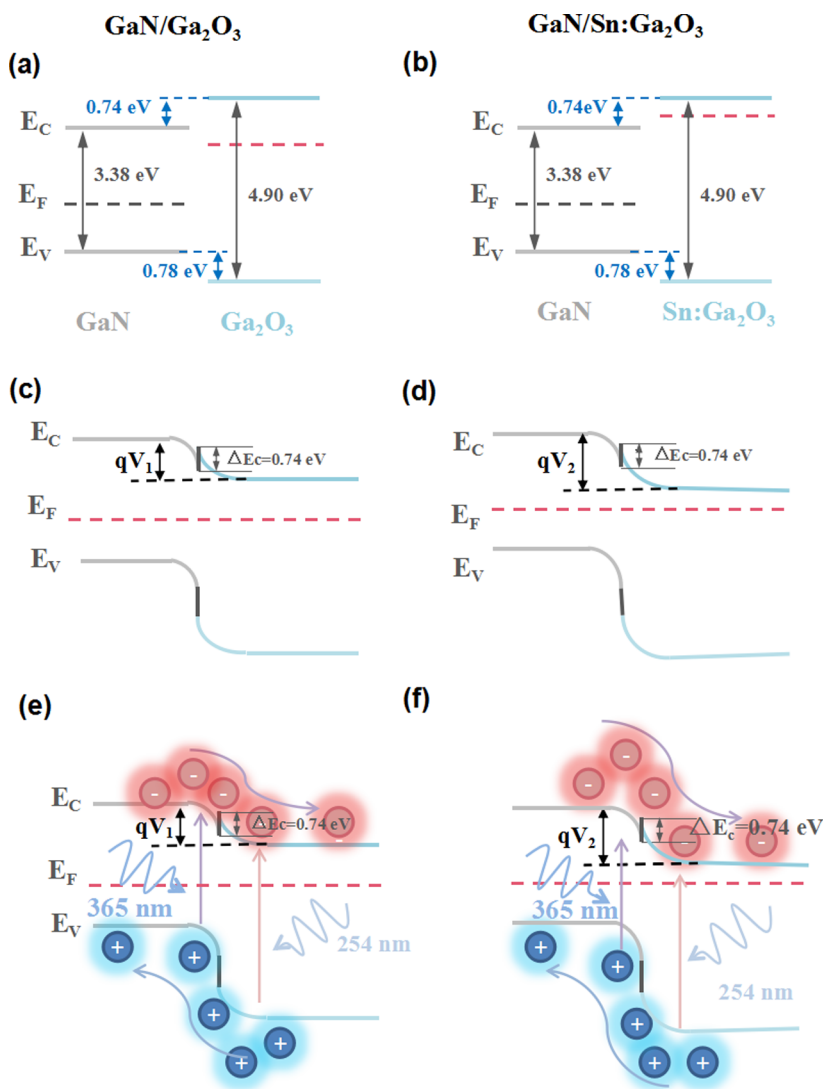
Figure 4. (a) Continuous time-dependent photoresponse of the GaN/Sn:Ga₂O₃ pn junction photodetector under zero bias at 254 and 365 nm illumination with a light intensity of 1000 $\mu\text{W}/\text{cm}^2$. (b) Time-dependent photoresponse of the photodetector under zero bias and 254 nm light with various light intensities. (c) Photocurrent and responsivity as a function of the light intensity. (d) Detectivity as a function of the light intensity. (e) Time-dependent photoresponse of the photodetector under various bias with 280 nm LED light illumination. (f) Wavelength selectivity of the photodetector under zero bias. (g) Photoresponse measurement configuration of the GaN/Sn:Ga₂O₃ pn junction photodetector. (h) Temporal pulse photoresponse of the photodetector excited by a 193 nm pulse laser for 50 pulses; (inset) enlarged view of the decay edge and the corresponding exponential fitting.

sensitivity, was calculated as previously shown by the following formula: $R = (I_{\text{photo}} - I_{\text{dark}})/(PS)$, where I_{photo} is the photocurrent, I_{dark} is the dark current, P is the supplied light intensity, and S is the effective area of the photodetector.^{31,32} In summary, the responsivity decreases as the light intensity

increases. When more electron–hole pairs are generated with a higher light intensity, self-heating will be induced, which not only increases charge carrier scattering but also increases the possibility of recombination. At 254 nm UV illumination with an intensity of 50 $\mu\text{W}/\text{cm}^2$, a maximum R of 3.05 A/W was

Table 1. Comparison of the Photoresponse Parameters of the GaN/Sn:Ga₂O₃ pn Junction UV Photodetector under Zero Bias from This Work and Other Previously Reported Self-Powered Devices

photodetector	wavelength (nm)	responsivity (mA/W)	$R_{\text{peak}}/R_{400 \text{ nm}}$ ratio	$I_{\text{photo}}/I_{\text{dark}}$ rejection ratio	rise time/decay time	detectivity [Jones]	ref
Au/Ga ₂ O ₃	258	0.01	38		1 μ s/100 μ s		13
diamond/ β -Ga ₂ O ₃	244	0.2	135	37			3
Ga ₂ O ₃ /NSTO	254	2.6		20	0.21 s/0.07 s		20
polyaniline/MgZnO	250	0.16	$\sim 10^4$		<0.3 s/<0.3 s	1.5×10^{11}	32
GaN/ZnO	358	0.68					34
n-ZnO/p-NiO	370	0.493			1.38 μ s/10 μ s		20
Ag/ZnMgO/ZnO	275	16	$\sim 10^4$		24 μ s/300 μ s	5×10^9	35
ZnO/Ga ₂ O ₃	251	9.7	6.9×10^2		100 μ s/900 μ s	6.3×10^{12}	14
GaN/Ga ₂ O ₃	254	28.44		80	0.14 s/0.07 s	6.2×10^{10}	22
GaN/Sn:Ga ₂ O ₃	254	3.05×10^3	5.9×10^3	6.1×10^4	0.018s	1.69×10^{13}	this work

**Figure 5.** Schematic energy band diagrams of the GaN/Ga₂O₃ and GaN/Sn:Ga₂O₃ pn junctions: (a, b) before contact; (c, d) dark conditions (after contact); (e, f) at 254 and 365 nm UV illumination (after contact), respectively.

obtained for the GaN/Sn:Ga₂O₃ pn junction photodetector. Currently, this is the highest reported value for self-powered UV photodetectors under zero bias. The detectivity (D) is a figure-of-merit of a photodetector, which usually describes the smallest detectable signal.^{33,34} The D of the GaN/Sn:Ga₂O₃ photodetector can be calculated using the calculation $D = R/$

$(2eJ)^{1/2}$ as previously described, where e is the elemental charge and J is the dark current density.^{34,35} The parameter D of the photodetector decreases as the light intensity increases and has a similar trend in responsivity, as shown in Figure 4(d). A maximum value of D of $1.69 \times 10^{13} \text{ cm} \cdot \text{Hz}^{1/2} \cdot \text{W}^{-1}$ was

obtained under $50 \mu\text{W}/\text{cm}^2$ 254 nm light illumination at zero bias, which reveals a high signal-to-noise ratio.

The influence of applied biases on the photoresponses of the GaN/Sn:Ga₂O₃ pn junction photodetector was also investigated under 280 nm LED light illumination (Figure 4(e)). The dark current (I_{dark}) increases rapidly from about 9.0×10^{-11} A to 2.1×10^{-7} A as the voltage jumps from 0 to 0.5 V, and then I_{dark} increases steadily as the voltage increases. Both I_{dark} and I_{photo} increase as the applied bias increases. The dark current increases when a higher bias is applied due to the faster drift velocity and the release of more carriers from oxygen vacancy traps. A higher photocurrent corresponds to higher bias, which can be attributed to an increase in photogenerated electron–hole pair separation. The ratio of $I_{\text{dark}}/I_{\text{photo}}$ decreases as the bias increases. The ratios at different biases are 1.2×10^4 , 11.9, 4.5, 2.3, 1.6, 1.3, and 1.1 at 0, 0.5, 1, 1.5, 2, 2.5, and 3 V, respectively.

The wavelength-dependent photoresponsivity of the GaN/Sn:Ga₂O₃ pn junction photodetector under zero bias was evaluated with LED illumination at wavelengths of 254, 280, 310, 365, 400, 450, 532, 635, and 905 nm. The results are shown in Figure 4(f). A maximum R of 3.05 A/W was obtained at 254 nm, which corresponds to the band gap of Ga₂O₃ (4.9 eV), implying that the photodetector presents an extremely high detectivity to weak solar-blind UV signals. The R exhibits a sharp jump between 365 nm ($R_{365 \text{ nm}} = 0.57$ A/W) and 400 nm ($R_{400 \text{ nm}} = 5.2 \times 10^{-4}$ A/W) light, which indicates that the self-powered photodetector is a UV photodetector. The UV/visible rejection ratio ($R_{254 \text{ nm}}/R_{400 \text{ nm}}$) of our GaN/Sn:Ga₂O₃ pn junction photodetector is about 5.9×10^3 , which represents high spectral selectivity of the UV region.

Furthermore, a special measurement system (Figure 4(g)) is constructed for fast-speed photon detection.³⁶ A 100 M Ω load resistor is in series with the GaN/Sn:Ga₂O₃ pn junction photodetector.³⁶ An oscilloscope records the bias change of the load resistor and monitors the current variation of the series circuit. Figure 4(h) shows the temporal pulse photoresponse of the photodetector continuously excited by a 193 nm pulse laser for 50 pulses. The dynamic response of the photodetector presents good stability and reproducibility. The photoresponse decay curve was fitted using a biexponential relaxation equation, $I = I_0 + Ce^{-t/\tau_1} + De^{-t/\tau_2}$, where I_0 stands for the steady state photocurrent, t represents the time, C and D are constants, and τ_1 and τ_2 are relaxation time constants.^{10,22} The inset of Figure 4(h) shows that the decay process is well fitted. The decay process consists of a fast-response component and a slow-response component, corresponding to a τ_{d1} of 18 ms and a τ_{d2} of 148 ms. Usually, the fast-response component is due to the rapid change of carrier concentration when the light is turned on/off; the slow-response component is due to the carrier trapping/releasing from defects.⁶

Comparison of the photoresponse parameters under zero bias of the GaN/Sn:Ga₂O₃ pn junction UV photodetector in this work and other previously reported self-powered devices is listed in Table 1.^{37,38} The GaN/Sn:Ga₂O₃ pn junction heterojunction UV photodetector shows a larger responsivity, detectivity, and $I_{\text{photo}}/I_{\text{dark}}$ ratio than those of other UV self-powered photodetectors. The UV/visible rejection ratio and photoresponse speed are comparable to those of the previously reported UV self-powered photodetectors.

Compared to the GaN/Ga₂O₃ junction, the GaN/Sn:Ga₂O₃ pn junction photodetector has improved substantially. In order to explain the microscopic photoinduced electrical conduction mechanism, energy band diagrams of the GaN/Ga₂O₃ and GaN/Sn:Ga₂O₃ heterojunctions are given in Figure 5. According to our previous work,²³ the band gap of GaN and Ga₂O₃ are 3.38 and 4.9 eV, respectively, and the valence band maximum are 1.58 and 4.05 eV, respectively. Thus, the valence band offset $\Delta E_v = 0.78$ eV and the conduction band offset $\Delta E_c = 0.74$ eV of the GaN/Ga₂O₃ heterojunction can be calculated. Figure 5(a) shows the diagram of the energy band of the GaN/Ga₂O₃ heterojunction. After contact, carriers can flow until both Fermi levels line up, and a pn junction depletion layer is formed near the interface of GaN/Ga₂O₃. The built-in potential barrier (qV) of the pn junction can be calculated using the difference between the work functions of GaN and Ga₂O₃. For the self-powered photodetector, the built-in potential barrier is the most important factor because the photogenerated carriers are separated only by the electric field under zero bias. The larger the value of qV , the better performance a photodetector has. Because the Fermi level of Sn-doped Ga₂O₃ is closer to the conduction band than that of pure Ga₂O₃ due to more free carriers (Figure 5(b)), the built-in potential barrier of the GaN/Sn:Ga₂O₃ junction (qV_2) is larger than that of the GaN/Ga₂O₃ junction (qV_1), as shown in Figure 5(c) and (d). When UV light irradiates the device, the light penetrates the electrode into the interface of the GaN/Ga₂O₃ heterojunction and generates electron–hole pairs. Under zero bias, the photogenerated electron–hole pairs in the depletion layer rapidly separate under the built-in electric field. The electrons transport toward n-type Ga₂O₃; the holes transport toward p-type GaN and then toward corresponding electrodes (Figure 5(e) and (f)). The Ga₂O₃ thin film is used as the window for penetrating UV light, and the n-type semiconductor for constructing the pn junction. The core workspace of the pn junction self-powered photodetectors is the depletion layer. The separation of the photogenerated carriers is more effective and faster with a larger built-in potential barrier. As a result, the GaN/Sn:Ga₂O₃ pn junction photodetector exhibits a better self-powered performance than the GaN/Sn:Ga₂O₃ photodetector.

CONCLUSIONS

In summary, the self-powered UV photodetectors were successfully built with a GaN/Ga₂O₃ pn junction through depositing an n-type Ga₂O₃ thin film onto an Al₂O₃ single-crystal substrate shielded by a p-type GaN thin film. Compared to the pure Ga₂O₃ film, the photoresponse of the GaN/Ga₂O₃ pn junction photodetectors based on Sn-doped Ga₂O₃ thin films has improved. The responsivity at 254 nm can reach up to 3.05 A/W with a high UV/visible rejection ratio ($R_{254 \text{ nm}}/R_{400 \text{ nm}} = 5.9 \times 10^3$) under zero bias. Additionally, the device exhibits a low dark current (1.8×10^{-11} A), a high $I_{\text{photo}}/I_{\text{dark}}$ ratio ($\sim 10^4$), an excellent detectivity rate ($1.69 \times 10^{13} \text{ cm}^2 \text{ Hz}^{1/2} \text{ W}^{-1}$), and a fast photoresponse time (18 ms). These improvements are attributed to the rapid separation of photogenerated electron–hole pairs driven by a built-in electric field in the interface depletion region of the GaN/Sn:Ga₂O₃ pn junction. The results reported in this study show the construction of a high-responsivity self-powered UV photodetector with potential applications in environmental monitoring, insecure communication, and space detection.

METHODS

Preparation and Characterization of Materials. The p-type Mg-doped GaN (Mg:Ga_{0.99}N) thin films with a thickness of 4 μm grown on *c*-plane (0001) Al₂O₃ were used as substrates (purchased from Suzhou Nanowin Science and Technology Co. Ltd.). The carrier mobility of GaN thin films is about 10 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. The n-type Sn-doped Ga₂O₃ thin film with a thickness of 375 nm was deposited on the GaN film by pulse laser deposition (PLD). A Ga₂O₃ ceramic disk with a Sn doping concentration of 2 at. % was used as the target. The chamber base pressure was 1×10^{-6} Pa. Optimal growth conditions were explored by ranging the temperature of the film growth from 600 to 750 $^{\circ}\text{C}$ and the oxygen pressure from 8×10^{-4} to 8×10^{-2} Pa. The laser ablation was performed using a 248 nm KrF excimer laser at a fluence of 4 J/cm^2 with a repetition rate of 2 Hz. A detailed preparation is described in early work.²³ The structure, crystallinity, and orientation of the as-grown thin films were characterized by XRD. The surface morphology was characterized by an FE-SEM and a Bruker-Veeco AFM.

Performance Test of Devices. For the performance test of the UV photodetector, Ag circular electrodes (0.5 mm diameter) with a thickness of 7 nm were deposited on both sides, the Sn:Ga₂O₃ thin film surface and the GaN film surface, respectively, as a semi-transparent electrode through a metal mask by radio frequency magnetron sputtering. A small point electrode (~ 0.1 mm diameter) of In metal was pressed onto the Ag circular electrode to obtain a region to connect Cu wires. A Keithley 4200 was used to measure the current–voltage (*I*–*V*) characteristics and time-dependent photoresponse of the fabricated device. The time-dependent photoresponse measurement was carried out through the use of a low-pressure mercury lamp at 254 nm with varying light intensities and applied biases. All experiments were performed at room temperature.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Chen, H.; Liu, K.; Hu, L.; Al-Ghamdi, A. A.; Fang, X. New Concept Ultraviolet Photodetectors. *Mater. Today* **2015**, *18*, 493–502.
- (2) Teng, F.; Hu, K.; Ouyang, W.; Fang, X. Photoelectric Detectors Based on Inorganic *p*-Type Semiconductor Materials. *Adv. Mater.* **2018**, *30*, 1706262.
- (3) Chen, Y. C.; Lu, Y. J.; Lin, C. N.; Tian, Y. Z.; Gao, C. J.; Dong, L.; Shan, C. X. Self-Powered Diamond/ β -Ga₂O₃ Photodetectors for Solar-Blind Imaging. *J. Mater. Chem. C* **2018**, *6*, 5727–5732.
- (4) Guo, D. Y.; Shi, H. Z.; Qian, Y. P.; Lv, M.; Li, P. G.; Su, Y. L.; Liu, Q.; Chen, K.; Wang, S. L.; Cui, C.; Li, C. R.; Tang, W. H. Fabrication of β -Ga₂O₃/ZnO Heterojunction for Solar-Blind Deep Ultraviolet Photodetection. *Semicond. Sci. Technol.* **2017**, *32*, 03LT01.
- (5) Chu, J. W.; Wang, F. M.; Yin, L.; Lei, L.; Yan, C. Y.; Wang, F.; Wen, Y.; Wang, Z. X.; Jiang, C.; Feng, L. P.; Xiong, J.; Li, Y. R.; He, J. High-Performance Ultraviolet Photodetector Based on a Few-Layered 2D NiPS₃ Nanosheet. *Adv. Funct. Mater.* **2017**, *27*, 1701342.
- (6) Guo, D. Y.; Wu, Z. P.; An, Y. H.; Guo, X. C.; Chu, X. L.; Sun, C. L.; Li, L. H.; Li, P. G.; Tang, W. H. Oxygen Vacancy Tuned Ohmic-Schottky Conversion for Enhanced Performance in β -Ga₂O₃ Solar-Blind Ultraviolet Photodetectors. *Appl. Phys. Lett.* **2014**, *105*, 023507.
- (7) Lin, R.; Zheng, W.; Zhang, D.; Zhang, Z.; Liao, Q.; Yang, L.; Huang, F. High-Performance Graphene/ β -Ga₂O₃ Heterojunction Deep-Ultraviolet Photodetector with Hot-Electron Excited Carrier Multiplication. *ACS Appl. Mater. Interfaces* **2018**, *10*, 22419–22426.
- (8) Cui, S.; Mei, Z.; Zhang, Y.; Liang, H.; Du, X. Room-Temperature Fabricated Amorphous Ga₂O₃ High-Response-Speed Solar-Blind Photodetector on Rigid and Flexible Substrates. *Adv. Opt. Mater.* **2017**, *5*, 1700454.
- (9) Li, Y.; Tokizono, T.; Liao, M.; Zhong, M.; Koide, Y.; Yamada, I.; Delaunay, J.-J. Efficient Assembly of Bridged β -Ga₂O₃ Nanowires for Solar-Blind Photodetection. *Adv. Funct. Mater.* **2010**, *20*, 3972–3978.
- (10) Guo, D. Y.; Wu, Z. P.; Li, P. G.; An, Y. H.; Liu, H.; Guo, X. C.; Yan, H.; Wang, G. F.; Sun, C. L.; Li, L. H.; Tang, W. H. Fabrication of β -Ga₂O₃ Thin Films and Solar-Blind Photodetectors by Laser MBE Technology. *Opt. Mater. Express* **2014**, *4*, 1067–1076.
- (11) Zheng, W.; Lin, R.; Ran, J.; Zhang, Z.; Ji, X.; Huang, F. Vacuum-Ultraviolet Photovoltaic Detector. *ACS Nano* **2018**, *12*, 425–431.
- (12) Zheng, W.; Lin, R.; Zhu, Y.; Zhang, Z.; Ji, X.; Huang, F. Vacuum Ultraviolet Photodetection in Two-Dimensional Oxides. *ACS Appl. Mater. Interfaces* **2018**, *10*, 20696–20702.
- (13) Luo, J. J.; Li, S. R.; Wu, H. D.; Zhou, Y.; Li, Y.; Liu, J.; Li, J. H.; Li, K. H.; Yi, F.; Niu, G. D.; Tang, J. Cs₂AgInCl₆ Double Perovskite Single Crystals: Parity Forbidden Transitions and Their Application For Sensitive and Fast UV Photodetectors. *ACS Photonics* **2018**, *5*, 398–405.
- (14) Chen, X.; Liu, K.; Zhang, Z.; Wang, C.; Li, B.; Zhao, H.; Zhao, D.; Shen, D. Self-Powered Solar-Blind Photodetector with Fast Response Based on Au/ β -Ga₂O₃ Nanowires Array Film Schottky Junction. *ACS Appl. Mater. Interfaces* **2016**, *8*, 4185–4191.
- (15) Zhao, B.; Wang, F.; Chen, H.; Zheng, L.; Su, L.; Zhao, D.; Fang, X. An Ultrahigh Responsivity (9.7 mA/W^{-1}) Self-Powered Solar-Blind Photodetector Based on Individual ZnO-Ga₂O₃ Heterostructures. *Adv. Funct. Mater.* **2017**, *27*, 1700264.
- (16) Li, X. Y.; Liu, W.; Li, P. G.; Song, J.; An, Y. H.; Shen, J. Q.; Wang, S. L.; Guo, D. Y. A Self-Powered Nano-Photodetector Based on PFH/ZnO Nanorods Organic/Inorganic Heterojunction. *Results Phys.* **2018**, *8*, 468–472.
- (17) Wu, Z.; Jiao, L.; Wang, X.; Guo, D.; Li, W.; Li, L.; Huang, F.; Tang, W. A Self-Powered Deep-Ultraviolet Photodetector Based on an Epitaxial Ga₂O₃/Ga:ZnO Heterojunction. *J. Mater. Chem. C* **2017**, *5*, 8688–8693.
- (18) Ma, N.; Zhang, K. W.; Yang, Y. Photovoltaic-Pyroelectric Coupled Effect Induced Electricity for Self-Powered Photodetector System. *Adv. Mater.* **2017**, *29*, 1703694.
- (19) Bai, F.; Qi, J. J.; Li, F.; Fang, Y. Y.; Han, W. P.; Wu, H. L.; Zhang, Y. A High-Performance Self-Powered Photodetector Based on Monolayer MoS₂/Perovskite Heterostructures. *Adv. Mater. Interfaces* **2018**, *5*, 1701275.
- (20) Chen, X.; Xu, Y.; Zhou, D.; Yang, S.; Ren, F. F.; Lu, H.; Tang, K.; Gu, S.; Zhang, R.; Zheng, Y.; Ye, J. Solar-Blind Photodetector with High Avalanche Gains and Bias-Tunable Detecting Functionality Based on Metastable Phase α -Ga₂O₃/ZnO Isotype Heterostructures. *ACS Appl. Mater. Interfaces* **2017**, *9*, 36997–37005.

- (21) Ni, P. N.; Shan, C. X.; Wang, S. P.; Liu, X. Y.; Shen, D. Z. Self-Powered Spectrum-Selective Photodetectors Fabricated from *n*-ZnO/*p*-NiO Core-Shell Nanowire Arrays. *J. Mater. Chem. C* **2013**, *1*, 4445–4449.
- (22) Guo, D. Y.; Liu, H.; Li, P. G.; Wu, Z. P.; Wang, S. L.; Cui, C.; Li, C. R.; Tang, W. H. Zero-Power-Consumption Solar-Blind Photodetector Based on β -Ga₂O₃/NSTO Heterojunction. *ACS Appl. Mater. Interfaces* **2017**, *9*, 1619–1628.
- (23) Li, P. G.; Shi, H. Z.; Chen, K.; Guo, D. Y.; Cui, W.; Zhi, Y. S.; Wang, S. L.; Wu, Z. P.; Chen, Z. W.; Tang, W. H. Construction of GaN/Ga₂O₃ *p-n* Junction for an Extremely High Responsivity Self-Powered UV Photodetector. *J. Mater. Chem. C* **2017**, *5*, 10562–10570.
- (24) Narita, T.; Kachi, T.; Kataoka, K.; Uesugi, T. P-type Doping of GaN by Magnesium Ion Implantation. *Appl. Phys. Express* **2017**, *10*, 016501.
- (25) Amano, H. Growth of GaN Layers on Sapphire by Low-Temperature-Deposited Buffer Layers and Realization of *p*-type GaN by Magnesium Doping and Electron Beam Irradiation. *Angew. Chem., Int. Ed.* **2015**, *54*, 7764–7769.
- (26) Pearton, S. J.; Yang, J. C.; Cary, P. H.; Ren, F.; Kim, J.; Tadjer, M. J.; Mastro, M. A. A Review of Ga₂O₃ Materials, Processing, and Devices. *Appl. Phys. Rev.* **2018**, *5*, 011301.
- (27) Guo, D. Y.; Qian, Y. P.; Su, Y. L.; Shi, H. Z.; Li, P. G.; Wu, J. T.; Wang, S. L.; Cui, C.; Tang, W. H. Evidence for the Bias-Driven Migration of Oxygen Vacancies in Amorphous Non-Stoichiometric Gallium Oxide. *AIP Adv.* **2017**, *7*, 065312.
- (28) Guo, D. Y.; Qin, X. Y.; Lv, M.; Shi, H. Z.; Su, Y. L.; Yao, G. S.; Wang, S. L.; Li, C. R.; Li, P. G.; Tang, W. H. Decrease of Oxygen Vacancy by Zn-doped for Improving Solar-Blind Photoelectric Performance in β -Ga₂O₃ Thin Films. *Electron. Mater. Lett.* **2017**, *13*, 483–488.
- (29) Dong, L. P.; Jia, R. X.; Xin, B.; Peng, B.; Zhang, Y. M. Effects of Oxygen Vacancies on the Structural and Optical Properties of β -Ga₂O₃. *Sci. Rep.* **2017**, *7*, 40160.
- (30) Rafique, S.; Han, L.; Neal, A. T.; Mou, S.; Tadjer, M. J.; French, R. H.; Zhao, H. Heteroepitaxy of *N*-type β -Ga₂O₃ Thin Films on Sapphire Substrate by Low Pressure Chemical Vapor Deposition. *Appl. Phys. Lett.* **2016**, *109*, 132103.
- (31) Zheng, W.; Huang, F.; Zheng, R.; Wu, H. Low-Dimensional Structure Vacuum-Ultraviolet-Sensitive ($\lambda < 200$ nm) Photodetector with Fast-Response Speed Based on High-Quality AlN Micro/Nanowire. *Adv. Mater.* **2015**, *27*, 3921–3927.
- (32) Guo, D. Y.; Li, P. G.; Wu, Z. P.; Cui, W.; Zhao, X. L.; Lei, M.; Li, L. H.; Tang, W. H. Inhibition of Unintentional Extra Carriers by Mn Valence Change for High Insulating Devices. *Sci. Rep.* **2016**, *6*, 24190.
- (33) Zhao, B.; Wang, F.; Chen, H. Y.; Wang, Y. P.; Jiang, M. M.; Fang, X. S.; Zhao, D. X. Solar-Blind Avalanche Photodetector Based on Single ZnO-Ga₂O₃ Core-Shell Microwire. *Nano Lett.* **2015**, *15*, 3988–3993.
- (34) Chen, H.; Yu, P.; Zhang, Z.; Teng, F.; Zheng, L.; Hu, K.; Fang, X. Ultrasensitive Self-Powered Solar-Blind Deep-Ultraviolet Photodetector Based on All-Solid-State Polyaniline/MgZnO Bilayer. *Small* **2016**, *42*, 5809–5816.
- (35) Liu, Y. T.; Jia, R. X.; Wang, Y. C.; Hu, Z. Y.; Zhang, Y. M.; Pang, T. Q.; Zhu, Y. J.; Luan, S. Z. Inhibition of Zero Drift in Perovskite-Based Photodetector Devices via [6,6]-Phenyl-C61-butyric Acid Methyl Ester Doping. *ACS Appl. Mater. Interfaces* **2017**, *9*, 15638–15643.
- (36) Zheng, W.; Zhang, Z. J.; Lin, R. C.; Xu, K.; He, J.; Huang, F. High-Crystalline 2D Layered PbI₂ with Ultrasoft Surface: Liquid-Phase Synthesis and Application of High-Speed Photon Detection. *Adv. Electron. Mater.* **2016**, *2*, 1600291.
- (37) Su, L.; Zhang, Q.; Wu, T.; Chen, M.; Su, Y.; Zhu, Y.; Xiang, R.; Gui, X.; Tang, Z. High-Performance Zero-Bias Ultraviolet Photodetector Based on *p*-GaN/*n*-ZnO Heterojunction. *Appl. Phys. Lett.* **2014**, *105*, 072106.
- (38) Fan, M. M.; Liu, K. W.; Chen, X.; Zhang, Z. Z.; Li, B. H.; Shen, D. Z. A Self-Powered Solar-Blind Ultraviolet Photodetector Based on a Ag/ZnMgO/ZnO Structure with Fast Response Speed. *RSC Adv.* **2017**, *7*, 13092–13096.