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Reliable self-powered highly spectrum-selective ZnO ultraviolet photodetectors

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Ultraviolet photodetectors (PDs) have been fabricated from p -ZnO:(Li,N)/ n -ZnO structures in this Letter. The PDs can operate without any external power supply and show response only to a very narrow spectrum range. The self-power character of the devices is due to the built-in electric field in the p - n junctions that can separate the photogenerated electrons and holes while the high spectrum-selectivity has been attributed to the filter effect of the neutral region in the ZnO:(Li,N) layer. The performance of the self-powered highly spectrum-selective PDs degrades little after five months, indicating their good reliability. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4839495>]

Ultraviolet (UV) photodetectors (PDs) have potential applications in a variety of fields such as biological and chemical analysis, flame sensing, communications, missile detection, and astronomical studies.^{1,2} Several types of PDs have been developed, such as photoconductive type,^{3–5} metal-semiconductor-metal PDs,^{6–8} Schottky photodiodes,^{9–11} and p - n junction PDs.^{12–15} Usually, an external bias is needed to separate the photo-generated electrons and holes in a photodetector. For the requirement of PDs that can work in long-term unattended circumstances, great efforts have been paid to self-powered devices that can function free of external power source.^{16–19} It is accepted that since the built-in electric field can separate electrons and holes, PDs fabricated from p - n junctions can meet the above requirements and work without external power source; thus, p - n junctions have been considered as an ideal structure for self-powered PDs.

ZnO, as an important semiconductor with a wide band gap, exhibits excellent photosensitive properties in UV spectrum region while it is almost transparent in visible region.^{20–23} With the above characters, ZnO-based p - n junction is deemed as an ideal candidate for self-powered UV PDs. Nevertheless, the report on such PDs is still very limited.¹⁹ It is well known that the undoped ZnO usually shows n -type conduction. Although some available p -type materials, such as p -GaN, p -NiO, p -SiC, p -Si, and p -GaAs, can be used to construct heterojunctions with n -ZnO,^{24–28} the large difference in bonding states and physical properties of the constituent materials in the heterojunctions will lead to many structural imperfections or defects. A reproducible method of growing stable p -type ZnO film is crucial for the realization of ZnO p - n junction PDs. Recently, we have realized p -type ZnO films with good stability and reliability by lithium (Li)-nitrogen (N) codoping method,^{29,30} which lay a solid ground for the realization of ZnO p - n junction structured self-powered UV PDs.

In this Letter, ZnO p - n junction structured UV PDs have been fabricated. The PDs can operate without external power supply and response only to a narrow UV region; that is, self-powered highly spectrum-selective UV PDs have been obtained.

The ZnO p - n junctions investigated in this Letter were grown in a VG V80H radio-frequency molecular beam epitaxy technique employing a -plane sapphire as the substrates. Prior to the growth, the sapphire substrates were treated at 600 °C for 30 min to clean the surfaces. The O source used for the growth of the ZnO films was radical oxygen gas cracked in an Oxford Applied Research plasma cell (Model HD25) at a fixed radio-frequency power of 300 W, and the Zn source was metallic zinc contained in Knudsen cell at 245 °C. The Li,N codoped ZnO films were grown by using nitric oxide gas (6N) as the O source and N dopant (note that the nitric oxide was also cracked in a plasma cell at a radio-frequency power of 330 W, and the Zn source and Li dopant by heating metallic zinc and lithium contained in individual Knudsen cells at 240 °C and 310 °C, respectively). In and Ni/Au layers deposited by vacuum evaporation were employed as contacts on the undoped and Li,N codoped ZnO layers, respectively. The electrical properties of the layers and the current-voltage (I - V) curve of the ZnO p - n junctions were measured in a Hall measurement system (Lakeshore 7707). The photoresponse of the ZnO:(Li,N)/ZnO structure was characterized using a lock-in amplifier, a Spex scanning monochromator, and a 150 W Xe lamp was employed as the illumination source for the photoresponse measurement. The optical transmittance and absorption of the layers were recorded in a Shimadzu UV-3101PC spectrophotometer.

The schematic illustration of the ZnO:(Li,N)/ZnO structure is shown in Fig. 1(a). The undoped ZnO layer exhibits n -type conduction as indicated by Hall measurement, and the electron concentration and Hall mobility are $4.8 \times 10^{16} \text{ cm}^{-3}$ and $16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Since the direct Hall measurement on the ZnO:(Li,N) layer will be interfered by the underneath n -ZnO layer, another ZnO:(Li,N) film was grown directly onto the a -plane sapphire substrates in the same

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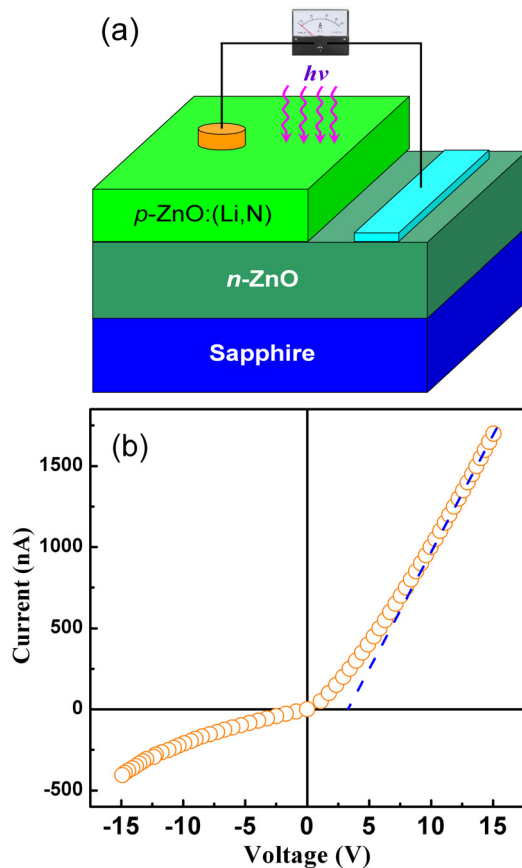


FIG. 1. The schematic illustration (a) and I - V curve (b) of the p -ZnO:(Li,N)/ n -ZnO structure.

growth process, and the electric properties of the film grown directly on sapphire substrate have been measured. The ZnO:(Li,N) layer shows p -type conduction, and the hole concentration and mobility are about $6.9 \times 10^{16} \text{ cm}^{-3}$ and $1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The thickness of the n -ZnO film is 530 nm, and that of the p -ZnO:(Li,N) is 120 nm. The I - V curve of the p -ZnO:(Li,N)/ n -ZnO structure is shown in Fig. 1(b). A perceptible rectifying behavior with a turn-on voltage of about 3.3 V can be observed from the curve.

To demonstrate the applicability of the ZnO p - n junction in UV PDs, the photoresponse of the structure has been measured, and the spectrum of which without any external power source is depicted in Fig. 2. The spectrum shows a dominant peak at around 380 nm. These results confirm that the ZnO homojunction can serve as a UV PD, and the PD can work without any external power source. Another noteworthy phenomenon in the photoresponse spectrum lies in the fact that the spectrum displays a very narrow width, whose full width at half maximum is only 9 nm, indicating that the PD only responds to a very narrow spectrum band. This characteristic makes the PD promising in some fields that need to monitor the photons in certain wavelength region.

The mechanism for the spectrum-selective response of the PDs has been detailed before.^{15,19} In the p -ZnO:(Li,N)/ n -ZnO structure, there will be two regions in the p -ZnO:(Li,N) layer at zero bias, that is, a depletion region near the p -ZnO/ n -ZnO interface and a neutral region in the top layer of the p -ZnO:(Li,N). The thickness of the depletion region in

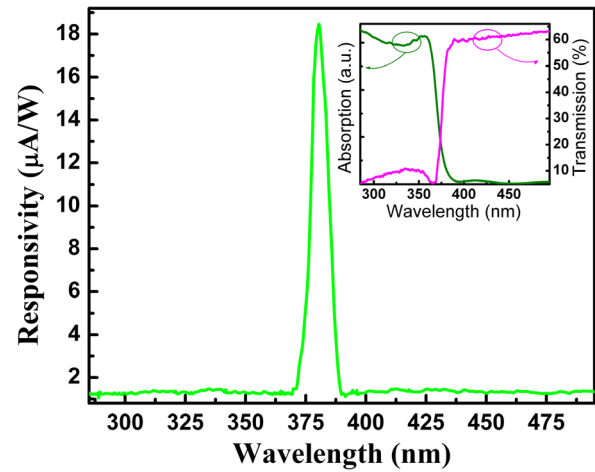


FIG. 2. Photoresponse of the p -ZnO:(Li,N)/ n -ZnO structured PDs without any external power source, and the inset shows the transmission spectrum of the p -ZnO:(Li,N) film and the absorption spectrum of the n -ZnO layer.

the p -ZnO:(Li,N) can be estimated from the following formula:³¹

$$W_{Dp} + W_{Dn} = \sqrt{\frac{2\epsilon_s}{q} \left(\frac{N_A + N_D}{N_A N_D} \right)} \psi_{bi}, \quad (1)$$

$$N_A W_{Dp} = N_D W_{Dn}, \quad (2)$$

where W_{Dp} is the width of the depletion region in the p -type side and W_{Dn} is the that in the n -type side, ϵ_s is the dielectric constant, q is the elemental electron charge, N_A is the acceptor concentration, N_D is the donor concentration, and ψ_{bi} is the potential barrier associated with the interface. By inserting all the known parameters into Eqs. (1) and (2), the depletion thickness in the p -ZnO:(Li,N) side can be determined to be around 55 nm. Considering that the total thickness of the p -ZnO:(Li,N) layer is about 120 nm, then the thickness of the neutral region in the p -ZnO:(Li,N) layer is around 65 nm. To understand the filter effect better, the transmission spectrum of the p -ZnO:(Li,N) film and the absorption spectrum of the n -ZnO film have been recorded, as shown in the inset of Fig. 2. One can see from the transmission spectrum that only the photons with their wavelength longer than around 370 nm can penetrate the ZnO:(Li,N) layer, while from the absorption spectrum one can see that only the photons with wavelength shorter than 390 nm can be absorbed by the underneath n -ZnO layer. Then the response of the p -ZnO:(Li,N)/ n -ZnO structure should lie in the range from 370 nm to 390 nm. Actually, one can see that the responsivity of the PDs lies just in this region, confirming that the high spectrum-selectivity comes from the filter effect of the neutral region in the ZnO:(Li,N) layer. Considering that the absorption coefficient α of a film can be expressed by the following formula:³²

$$\alpha = \frac{\ln(1/T)}{d}, \quad (3)$$

where T is the transmittance and d is the film thickness. One can see from the transmission spectrum of the ZnO:(Li,N) film that the transmittance at around 370 nm is around 5%,

then the absorption coefficient α can be derived to be $4.6 \times 10^5 \text{ cm}^{-1}$ from Eq. (3) considering that the thickness of the neutral region is around 65 nm. The transmission of photons in a material can be expressed by the following formula: $I = I_0 \exp(-\alpha d)$. In this expression, I_0 is the intensity of incident light, α is the absorption coefficient, and d is the propagation depth of the photons in the material. Considering that $\alpha = 4.6 \times 10^5 \text{ cm}^{-1}$, $d = 65 \text{ nm}$, then only around 5% of the photons with their wavelength shorter than 370 nm can penetrate the neutral region (65 nm) of the ZnO:(Li,N) layer. Since no external power source has been applied onto the p - n junctions, the electric field in the neutral region is nearly zero; thus, the carriers generated by the absorption of the photons in the neutral region will contribute little to the response of the PDs.^{33,34} The above result reveals that the neutral region in the p -ZnO:(Li,N) layer can really act as a filter that can filtrate the photons with their wavelength shorter than 370 nm. When the photons with wavelength longer than 370 nm penetrate the neutral layer and reach the depletion region of the p -ZnO:(Li,N)/ n -ZnO structure, the photons with their wavelength shorter than 390 nm will be absorbed by the depletion region, and electrons and holes will be generated there. Excitons formed by the columbic interaction of electrons and holes will be drifted to the p -ZnO:(Li,N)/ n -ZnO interface, and the photogenerated electrons will be drifted towards the n -ZnO side while the holes towards the p -ZnO side by the built-in electric field. In this way, the excitons will be dissociated, and photoresponse signals will be detected from the p -ZnO:(Li,N)/ n -ZnO structures.

It is rational to speculate that if a negative bias is applied onto the junction, the thickness of the depletion region in the p - n junction will be increased, thus the thickness of the neutral layer that acts as the filter will be decreased, and then the selectivity of the PD will be deteriorated. To test the above speculation, a series of negative biases have been applied onto the p - n junction, and the photoresponse spectra of the PD under the biases have been measured, as shown in Fig. 3. It can be seen from the figure that at 3 V bias, the response of the PD in the wavelength range from 250–370 nm increases significantly compared with that of the PD without any bias shown in Fig. 2. With further increasing the bias

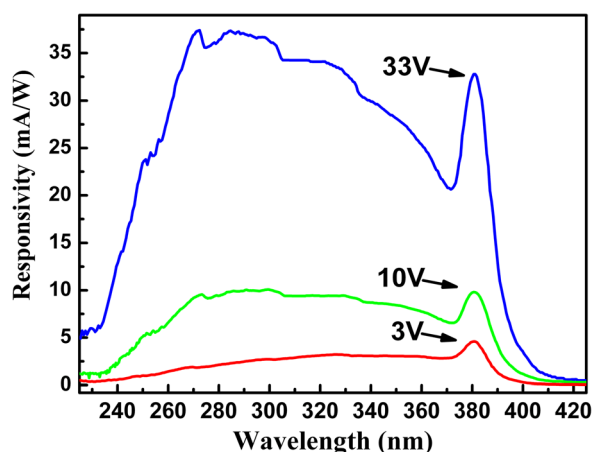


FIG. 3. Photoresponse of the p -ZnO:(Li,N)/ n -ZnO structured PDs at a reverse bias of 3 V, 10 V, and 33 V.

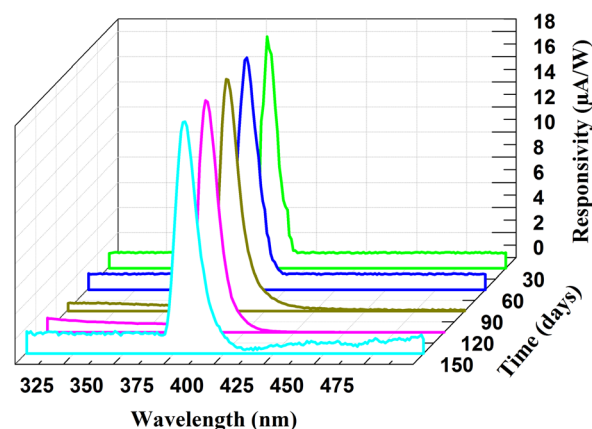


FIG. 4. Photoresponse of the p -ZnO:(Li,N)/ n -ZnO structure without any external power source recorded intermittently for five months.

voltage, the response in this region increases further. The above fact confirms that the spectrum-selectivity of the ZnO p - n junction PDs is caused by the filter effect of the neutral region in the ZnO:(Li,N) layer.

As mentioned before, self-powered devices have the advantage of working in long-term unattended circumstances, and then the reliability of these devices will be very important. In order to evaluate the reliability of the self-powered high spectrum-selectivity UV PDs, the response spectrum of the device without any external power source has been recorded intermittently. As shown in Fig. 4, the responsivity of the PDs degrades little in the investigated five months. The above result indicates that the self-powered UV PDs possess good reliability, which is favorable for their operation in long-term unattended circumstances.

In conclusion, p -ZnO:(Li,N)/ n -ZnO structured UV PDs have been developed. The PDs show response only to a narrow spectrum region, which can be attributed to the filter effect of the neutral region in the ZnO:(Li,N) layer. The PDs can work without any external power supply since the built-in electric field in the p - n junctions will separate the photogenerated electrons and holes. The self-powered spectrum-selective PDs degrade little in five months, indicating their good reliability. The results reported in this Letter may provide a clue for the potential applications of ZnO-based PDs in long-term unattended circumstances.

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