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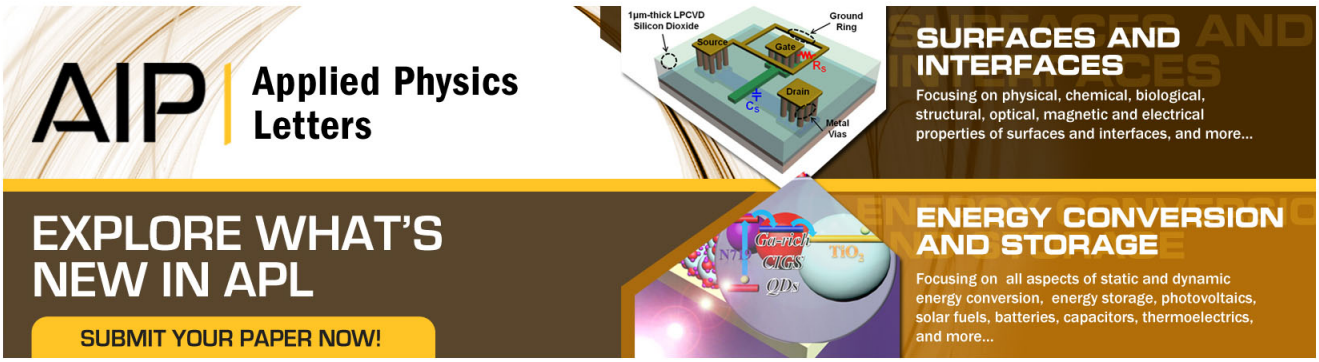

Wavelength selective p-GaN/ZnO colloidal nanoparticle heterojunction photodiode

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An ultraviolet heterojunction photodiode consisting of epitaxially grown p-GaN layers and polyvinyl alcohol coated ZnO colloidal nanoparticles exhibits a lowpass and bandpass alternative property depending on the illumination direction. At 0 V bias, a time response on the order of 10 s of milliseconds was demonstrated with a responsivity on the order of mA/W with about 100 nW of ultraviolet illumination. The rectification ratio at ±5 V was 1000 under dark environment. Deposition of colloidal ZnO nanoparticles on an independent p-GaN substrate introduces a technique to create a heterostructure pn junction photodiode with wavelength selection by back illumination. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4793210]

As a wide bandgap material with high exciton binding energy, zinc oxide (ZnO) is suitable for ultraviolet (UV) detection.[1–8] The most prominent issue hindering the development of ZnO UV devices is the lack of a reproducible p-type material.[9] As an intrinsic n-type material, majority carrier devices, such as photoconductors and metal-semiconductor-metal (MSM) photodetectors based on ZnO colloidal nanoparticles (NPs) coated with polyvinyl alcohol (PVA) have been investigated in the previous work.[10,11] PVA coated ZnO (PVA-ZnO) colloidal nanoparticles on epitaxially grown intrinsic AlGaN and GaN substrates to produce wavelength selectivity have also been reported.[12] The deposition of colloidal nanoparticles on an independent p-GaN substrate that exploits its semiconducting properties has yet to be accomplished. In recent literature, two devices with ZnO epitaxial layers and nanorods were grown on p-GaN to create a pn junction via molecular beam epitaxy (MBE) and vapor-liquid-solid (VLS) growth, respectively.[13,14] In this paper, PVA-ZnO NPs are spin coated on Mg doped p-GaN to form a heterojunction photodiode with the advantages of faster transient response and ease of manufacture.

The schematic diagram and band diagram of the p-GaN/PVA-ZnO NPs heterojunction photodiode are shown in Figures 1(a) and 1(b), respectively. The bandgap properties follow those previously used for ZnO nanostructures.[15,16] The p-GaN substrate purchased from Sensor Electronic Technology (SETI) has a 0.5 μm thick layer doped with magnesium with a doping concentration of about 2–4 $\times 10^{17}$ cm^{-3}, which is on top of a 3 μm semi-insulating GaN buffer layer and a 330 μm double side polished c-plane sapphire.

A gold contact was deposited on p-GaN using e-beam evaporation with a thickness of 200 nm followed by rapid annealing in O_2 at 500 °C for 1 min. The ZnO nanoparticles created by top-down wet-chemical synthesis described in previous work[10] (the XRD and SEM images are shown in Figures 2(a) and 2(b), respectively) were spin-coated onto the p-GaN with a thickness about 1 μm. A 200 nm Al contact was deposited by e-beam through a shadow mask on top of the ZnO nanoparticle thin film. Wires were bonded using a conductive epoxy to the gold and Al contacts.

The electrical characteristics of this heterojunction pn diode were measured under darkness and illumination by a 280 nm LED with optical intensity about 42.85 mW/cm^2. The heterojunction showed a diode-like I-V curve following good exponential fitting for the dark current, as presented in Figure 3. With forward bias, the current increases exponentially as the applied voltage increases with a turn on voltage about 3.65 V. The reverse saturation current is determined to be ~1 nA at 0 V though the minimum reverse current reaches ~1 pA at −3 V. The rectification ratio is about 1000 at ±5 V and the ideality factor is about 29 extracted from the fitting curve. A large ideality factor is common for heterostructure devices. Specifically, the large ideality factor may be explained by the interfacial disorder of the nanoparticles layer with Frenkel-Poole conduction properties.[17]

The UV photoresponse of the heterojunction photodiode was investigated by front illuminating (as shown in Figure 1) the pn junction with the 280 nm UV LED. Upon UV illumination, a significant current increase in the reverse bias region is observed. The UV generated current to dark current ratio is about 26 at −5 V. When forward biased, the photocurrent to dark current ratio is close to 1 as demonstrated in Figure 3(b). Under reverse bias, the drift current is controlled by minority carriers and therefore dominates the total current. But the hole concentration in intrinsic PVA coated ZnO nanoparticles is very low, while the electron concentration in p-GaN is also low (about 10^3 cm^{-3}). Under UV illumination, the generated e-h pairs dominate the total current. Under forward bias, the hole diffusion current from the p-GaN dominates the total current. This photoresponse is typical of a photodiode.

The time response of this detector was measured by using an oscilloscope to record the time-resolved photogenerated current with and without UV LED illumination under different biases which is then amplified with a gain at 10^8 A/V. As shown in Figure 4(a), as the bias increases, the rise time remains the same while the fall time significantly increases

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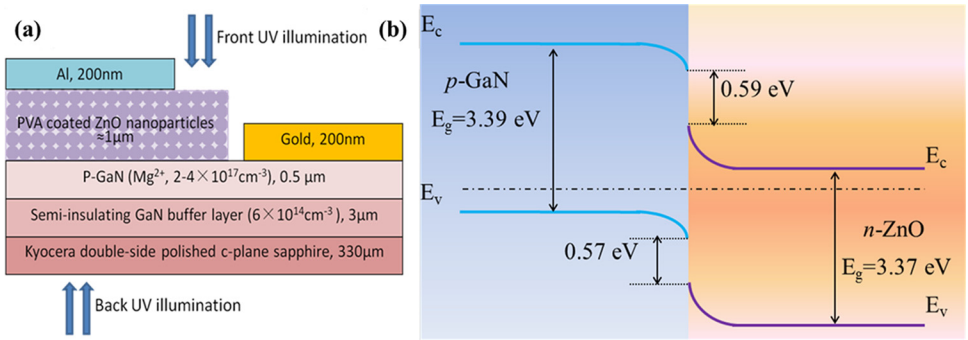

FIG. 1. (a) Schematic diagram and (b) band diagram of p-GaN/PVA-ZnO NPs heterojunction diode.

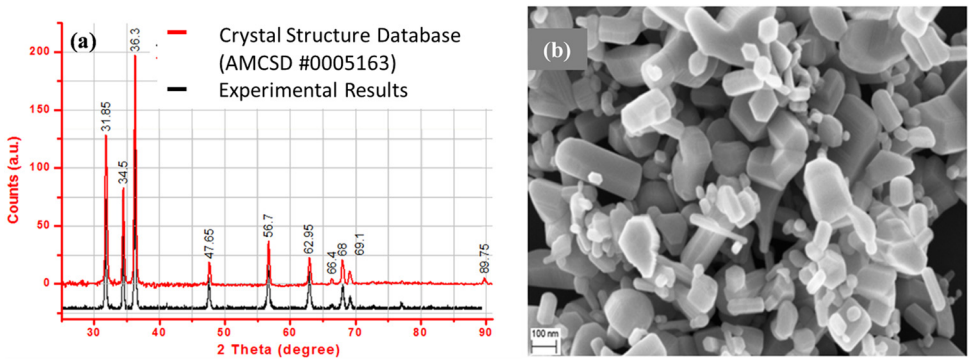

FIG. 2. (a) XRD patterns and (b) high resolution SEM results (100 nm) of PVA coated ZnO nanoparticles created by top-down wet-chemical etching method with an average size of 80 nm.

with increasing generated current. This is due to a higher electric field, resulting in a wider depletion region where more e-h pairs are generated. In addition, negatively charged oxygen ions at the nanoparticles' surfaces neutralize the photogenerated holes and leave excess conduction-band electrons, causing the accumulation of conduction electrons.[18–21] Once the light is turned off, the accumulated e-h pairs in traps are released under electrical field. But the conductivity of PVA coated ZnO nanoparticles is very low and the release time of the trapped carriers is an oxygen related process, making the decay time even longer when there are more generated e-h pairs. As indicated in Figure 4(b), the best time response of this pn photodiode is at 0 V bias, with a rise time (10%–90%) of 25 ms and the fall time (10%–90%) of 50 ms. The results are about 3 orders improvement compared to a photoconductor[22] and 1 order improvement compared to the MSM photodetector[11] based on the PVA-ZnO NPs. In comparison to a p-GaN, ZnO nanowire photodiode, about a 3 order of magnitude improvement is demonstrated.[13] However, these nanostructure devices are significantly slower than standard pn junction GaN p-i-n photodiodes built to reduce capacitance for ultrafast signal detection with response times on the order of 1 ns.[23]

The wavelength response of this heterojunction photodiode was measured with light having intensity on the order of 100 nW illuminated from front and back sides (as shown in Figure 1) under 0 V bias. As shown in the band diagram in Figure 1(b), the bandgap and electron affinity of p-GaN and ZnO are relatively close, making a small bandgap offset. Once the UV light is turned on, the photogenerated current dominates the total current through diffusion. The peak responsivity at 350 nm is about 0.225 mA/W when the optical power is 120 nW. The results show that small signal detection is possible with this photodiode. The responsivity is twice that of an epitaxially grown p-GaN/ZnO heterojuction for UV detection with a peak at 374 nm.[14] However, it is still less than the ultrafast standard pn junction GaN p-i-n photodiode mentioned above with a demonstrated peak responsivity of 30 mA/W at ~365 nm with −5 V bias.[23] Although the absolute responsivity is small, with the benefit of significantly

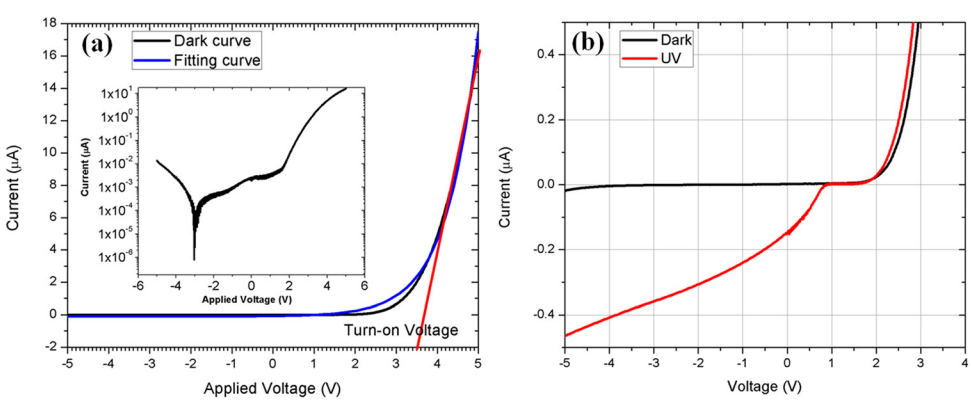

FIG. 3. (a) Dark current and its exponential fitting of p-GaN/PVA coated ZnO colloidal nanoparticles heterojunction as well as the inset of (a) dark current plotted in log scale, (b) its I-V plot under darkness and front illumination of 280 nm LED with optical intensity of 42.85 mW/cm^2.

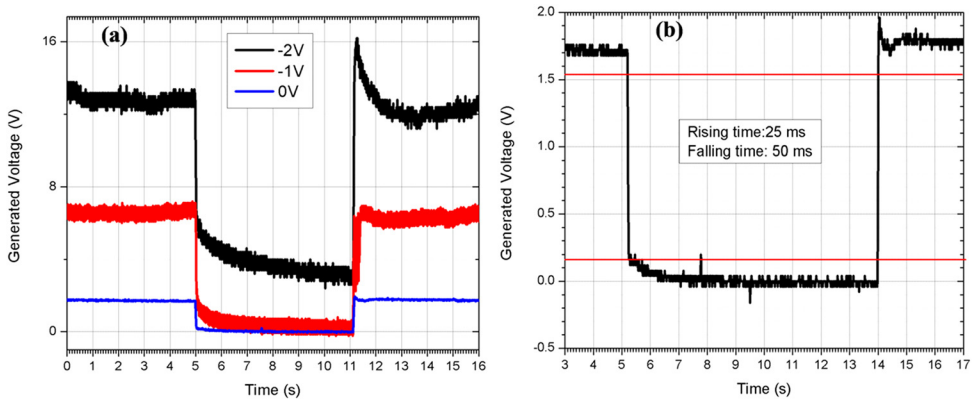

FIG. 4. Time response of p-GaN PVA-ZnO NPs heterojunction (a) shows bias dependence and (b) at 0 V bias the fastest response is achieved with 25 ms rising time and 50 ms falling time under back illumination.

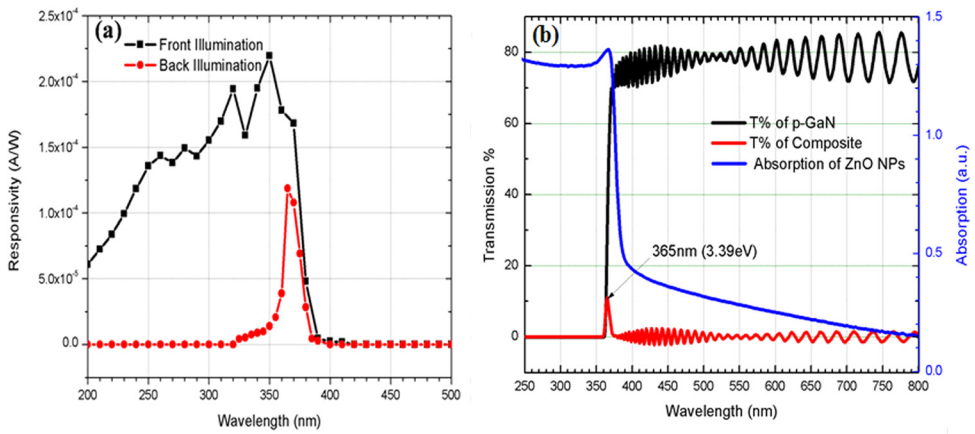

FIG. 5. (a) Wavelength response of p-GaN/PVA-ZnO NPs heterojunction illuminated from front (black square) and back (red circle) sides under 0 V bias, and (b) transmission and absorption spectra of Mg doped p-GaN show a cut-off wavelength at 365 nm.

improved time response, device design toward circumventing the tradeoff between response time and sensitivity is the future work. For example, a completely depleted vertical Schottky device structure has been studied to increase the time response while maintaining the good photoconductive performance of lead sulphide (PbS) nanoparticles photodetectors.[24] Methods to improve the conductivity of ZnO nanoparticles through carrier transfer to metal/semimetal materials and also plasmonic enhancement will be investigated.

The photoresponsivity spectrum in Figure 5(a) shows a lowpass response when the light is incident from the front side and a bandpass response when back illuminated. Under front illumination, the UV light with wavelength shorter than the bandgap of ZnO is absorbed and contributes to the photocurrent. While under back illumination, the light with wavelength shorter than the bandgap of GaN is completely absorbed by the 3 μm semi-insulated GaN (as indicated in the transmission curve in Figure 5(b)) which has an absorption coefficient about 11.31 μm^{-1} at 320 nm). These absorbed photons do not generate current since the absorption usually happens on the near bottom surface of GaN which is far from the contacts. When the light with wavelength longer than the bandgap of GaN, light will penetrate GaN and then arrive at ZnO to generate e-h pairs resulting in photocurrent. The result is a narrow, wavelength selective UV response.

In conclusion, a fast, lowpass, and bandpass alternative heterojunction photodiode was fabricated with the composition of Mg-doped p-GaN and PVA-ZnO NPs for small UV signal detection. At 0 bias, the peak responsivity at 350 nm is about 0.225 mA/W when the incident optical power is 120 nW. The time response on the order of 10 s of ms for this photodiode structure demonstrated 3 orders improvement compared to a photoconductor and 1 order improvement compared to the MSM photodetector based on the PVA-ZnO NPs. In comparison to a p-GaN, ZnO nanowire photodiode, about a 3 order of magnitude improvement is demonstrated. The rectification ratio is about 1000 at ± 5 V and the ideality factor is about 29 extracted from the fitting curve. A turn on voltage of about 3.65 V was demonstrated with the reverse saturation current of $\sim$1 nA at 0 V. This work provides an alternative method to creating a pn junction diode using PVA coated solution processed nanoparticles while providing wavelength selective, fast UV response.

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