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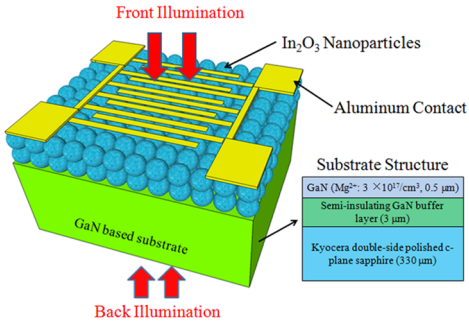

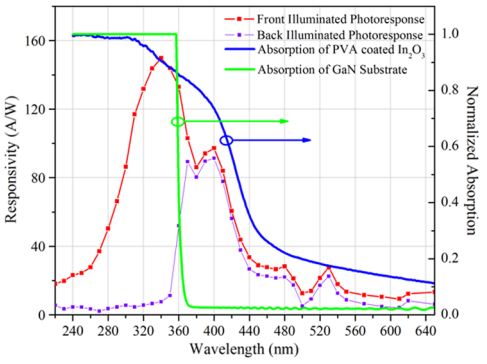

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High Responsivity, Bandpass Near-UV Photodetector Fabricated From PVA-In_2O_3 Nanoparticles on a GaN Substrate

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Abstract: High photoresponsivity in the near-ultraviolet (UV) range was observed for a photodetector fabricated from polyvinyl-alcohol (PVA)-coated In_2O_3 nanoparticles. The high responsivity is due to large depletion region introduced by ion-adsorbed oxygen on the surface of In_2O_3 nanoparticles. Experiments demonstrated that the photodetector exhibited either a low-pass or bandpass spectral response, depending on the illumination directions. Transient characteristics of photoconductivity have been studied, which shows a rise time of 700 s and a fall time of 1350 s.

Index Terms: In_2O_3 nanoparticles, ultraviolet (UV) detection, high gain.

1. Introduction

Ultraviolet (UV) photodetectors have a wide range of applications such as flame sensing, biological research, optical communication and missile launch detection. Currently, the most common devices for UV detection are "UV-enhanced" silicon photodiodes. However, "UV-enhanced" silicon photodiodes exhibit some inherent limitations: the requirement for filters to block visible and infrared photons, and degradation of devices on exposure to UV light with energies much higher than the semiconductor bandgap.

Wide band gap semiconductors such as GaN, ZnO, TiO_2 and diamond [1]–[7] have been widely studied due to their promising advantages such as intrinsic "visible-blindness" and high sensitivity at room-temperature operation. Yet only a few UV photodetectors are fabricated from In_2O_3 nanoparticles [8]. In this paper, we report a high responsivity near-UV photodetector fabricated from polyvinyl-alcohol (PVA)-coated In_2O_3 nanoparticles on an epitaxially grown, GaN substrate.

2. Experimental Details

The photodetector was fabricated from commercial In_2O_3 nanoparticles (US Research Nanomaterials Inc) with a purity of 99.995% and sizes ranging from 20–70 nm. They were surface treated with PVA solutions (1% in weight in water), which provide surface passivation. The PVA-coated In_2O_3 nanoparticles were centrifuged and dispersed in ethanol to form a suspension with concentration at 40 mg/ml. The solution was then spin-coated onto GaN substrate [grown by Sensor Electronic Technology Inc (SET Inc.)] and annealed in air at 120 °C for 5 min. Aluminum (Al) contacts were deposited on top of the In_2O_3 nanoparticles by using E-beam evaporation through a shadow mask. The Al contacts had a thickness of about 250 nm and were patterned as interdigitated fingers. The

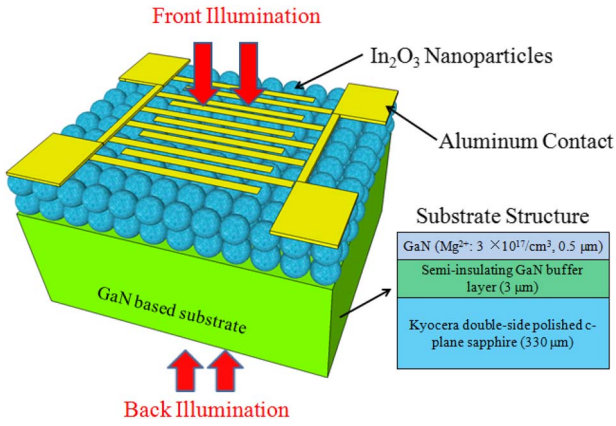

Fig. 1. Three-dimensional view of UV-Violet Photodetector fabricated from PVA-coated In_2O_3 nanoparticles on top of GaN substrate.

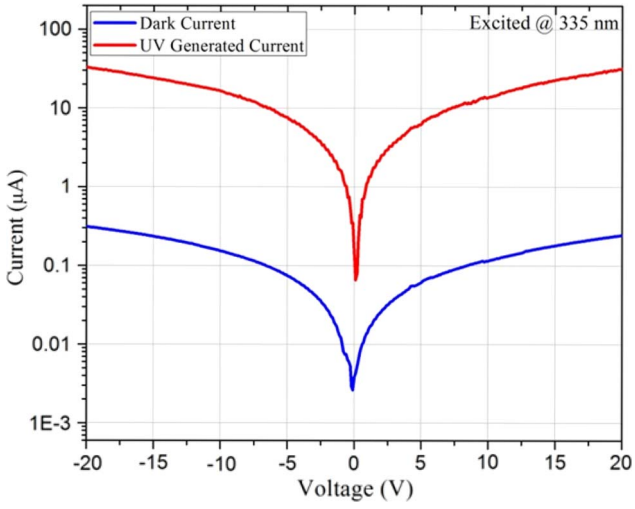

Fig. 2. Photocurrent and dark current of the photodetector measured as a function of bias voltages. The *I–V* plot shows the photocurrent to dark current ratio as high as 2 orders when biased at 20 V.

interelectrode distance (diagonal) is approximately 4 mm. Finally, the photodetector was packaged and wire bonded using Epo-Tek H20E conductive epoxy. The 3-D view of the fabricated photodetector has been shown in Fig. 1. The PVA-coated In_2O_3 nanoparticles exhibited enhanced UV optical performance proving PVA can effectively suppress the parasitic green emission for In_2O_3 nanoparticles. The detailed discussion of PVA passivation effect will be present in another work [9]; a similar effect has been observed for ZnO nanoparticles in our previous work [10].

3. Results and Discussion

Fig. 2 shows the typical *I–V* characteristic of the near-UV photodetector measured under darkness and 31.65 mW/cm^2 UV light illumination (335 nm). As seen from this figure, the photocurrent is about two orders of magnitude larger than the dark current in the entire bias voltage range of ±20 V.

The responsivity (front illumination) of the detector in near-UV range was measured at room temperature for different bias voltages, as shown in Fig. 3. The spectra show two major peaks located at 340 nm (3.65 eV) and 400 nm (3.09 eV), respectively. The 3.65 eV peak is close to the former bandgap of In_2O_3, believed to be 3.75 eV. The peak observed at 3.09 eV is also of interest.

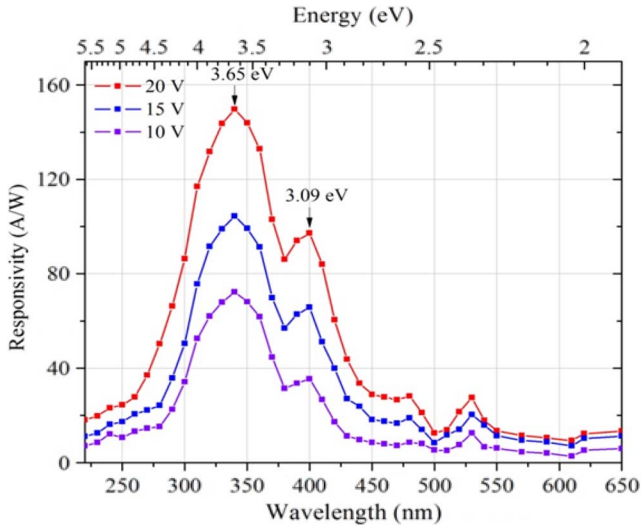

Fig. 3. Responsivity of photodetector measured under front illumination with different bias voltages.

Recent studies about the band structure of In_2O_3 indicate a near fundamental band gap near this peak at 2.93 $\pm$ 0.15 eV [11], [12]. Strong optical transitions are observed between the conduction band minimum and an energy state about 0.8 eV below the valence band maximum, aligning with the former bandgap value [11]. Optical transitions within the range 0–0.8 eV from the valance band maximum are weak due to a minimal dipole intensity that is a result of symmetry. Therefore, a lower responsivity at 3.09 eV is expected when compared to the responsivity around 3.65 eV. The photoresponsivity spectrum shows a broad band from 270 to 450 nm. Due to the morphology and the resulting surface defects of In_2O_3 nanoparticles, oxygen vacancies create various defect states within the band gap. Thus, the Fermi energy levels of these In_2O_3 nanoparticles are filled by electrons into many separate energy states [11], which will provide transition paths for carriers and leading to broadband photoresponsivity [13].

The responsivity of the device, defined as photocurrent per unit incident optical power, has been determined to be approximately 149 A/W at 340 nm and 97 A/W at 400 nm. For comparison, the responsivity for most commercial UV photodetectors is in the range of 0.1 to 0.2 A/W [14]. Such a high responsivity is mainly attributed to a two step mechanism that alters the width of the depletion region formed between the two contacts. The two steps of the mechanism are adsorption and desorption of oxygen molecules on the surface of In_2O_3, nanoparticles, which are presented in Fig. 4 [8], [15]. First, due to the affinity between the oxygen molecules and electrons, oxygen molecules adsorb onto In_2O_3 surface and capture nearby electrons to form negative charged oxygen ions layer. This process can be represented by $O_2(g) + e^- O_2^-$, which leads to a formation of depletion region near the surface and therefore a decrease of free carrier concentration inside In_2O_3 nanoparticles. The depletion region created in the oxygen adsorption process can extend throughout the entire film due to the high surface to volume ratio of in_2O_3 nanoparticles. Second, upon exposure to UV light, photogenerated holes can migrate to the surface of In_2O_3 nanoparticles and recombine with the negative charged oxygen ions $[h^+ + O_2^-(ad)\ O_2]$, resulting in a decrease in the width of the depletion region and increase in the free carrier concentration. Therefore, these two steps contribute to the large gain of the photodetectors. Moreover, the gain mechanism is dependent on the comparison of the transit time between electrodes and the carrier lifetime. If the transit time is less than the carrier lifetime gain occurs. With surface absorbed oxygen, the increase of electron lifetime may accentuate the traditional gain mechanism found in photoresistors.

It is worth mentioning that a recent study demonstrated high-quality single-crystalline material with an accumulation of electrons occurring at the (001) surface [16] rather than depletion. However, due to the large surface to volume ratio of In_2O_3 nanoparticles in this study, it is entirely

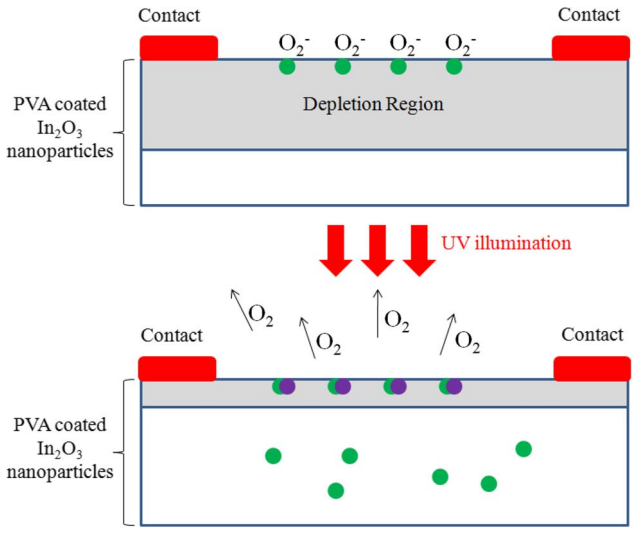

Fig. 4. Two mechanisms that contribute to the high responsivity of the bandpass photodetector fabricated from PVA-coated In_2O_3 nanoparticles. Upon UV illumination, the Schottky barrier height and the width of the depletion region decreased. Green Dots = electrons. Purple Dots = holes.

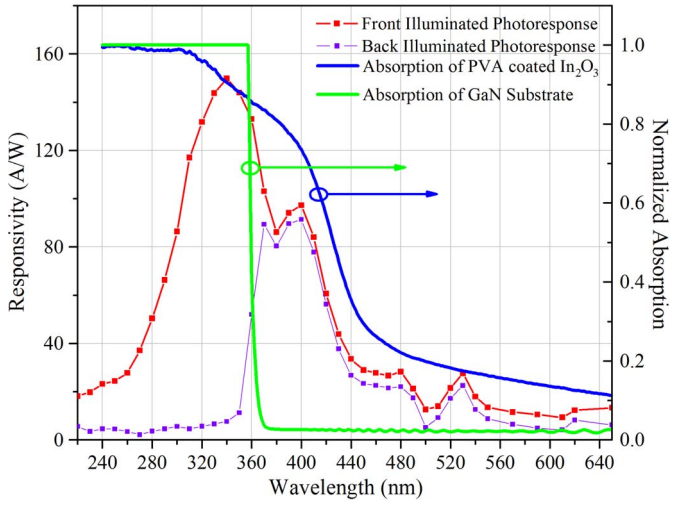

Fig. 5. Responsivity measured from back and front illuminated photoconductor, exhibiting bandpass (purple spectral: 360–450 nm) responsivity as it relates to the absorption spectra of GaN (green line) and PVA-coated In_2O_3 nanoparticles (blue line).

possible that the surface oxygen adsorption effect is prominent and the entire structure can be depleted.

Under front illumination, the photodetector exhibited a normal low-pass responsivity corresponding to the absorption cutoff wavelength of PVA-coated In_2O_3 nanoparticles. Under back illumination, light with wavelength shorter than 360 nm (cutoff wavelength of GaN) is absorbed by the GaN substrate. Electron-hole pairs generated within the GaN substrate do not generate current since these carriers do not have a conduction path to the contacts deposited on top of In_2O_3 nanoparticles. Thus the photodetector exhibited a bandpass photoresponsivity ranging from 360 nm to 480 nm, which has been shown in Fig. 5. $Al_xGa_{1-x}N$ substrate can also be applied to the device and the advantage is that the lower limit of the cutoff wavelength can be tuned within the range from 300 nm to 360 nm by changing the Al fraction in the substrate.

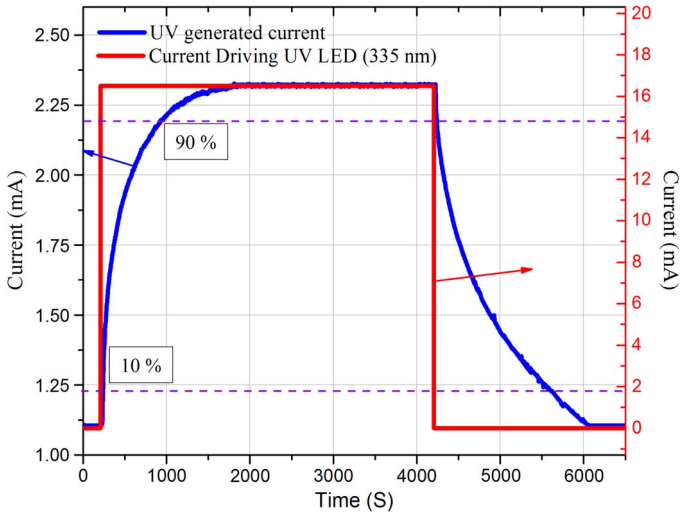

Fig. 6. Time resolved photocurrent measured for photodetector fabricated from PVA-coated In_2O_3 nanoparticles.

The time resolved photocurrent measured for this bandpass photodetector has been presented in Fig. 6. The rise time (from 10% to 90%) and fall time (from 90% to 10%) are 700 s and 1350 s, respectively. The rise time and fall time consists of two exponentials with different slopes: the first corresponds to the initial fast response (relative to magnitude 10–30%), and the second to the slower response (relative to magnitude 70%–90%) (see Fig. 5). The rise time curves may be represented as [15]

$$I_{\text{rise}} = I_0\left[1 - a_1\exp\left(-\frac{t}{\tau_1}\right) - a_2\exp\left(-\frac{t}{\tau_2}\right)\right]$$

and for fall time

$$I_{\text{fall}} = I_1\left[a_3\exp\left(-\frac{t}{\tau_3}\right) + a_4\exp\left(-\frac{t}{\tau_4}\right)\right]$$

where a1, a2, a3, and a4 represent numerical constants, and τ1, τ2, τ3, and τ4 are time constants. By fitting the expression with the rise and fall time curve, τ1, τ2 have been determined as 60.7 s and 416.4 s, respectively. The fitting results show that the value of τ3 is very close to τ4 (both are about 964 s), and thus, the expression for Ifall can be simplified as

$$I_{\text{fall}} = I_1 a_5\exp\left(-\frac{t}{\tau_3}\right).$$

The initial fast rising of the photocurrent with UV illumination can be explained by the release of the surface-adsorbed oxygen molecules to the air which results in a sharp increase in carrier concentration along with an improvement of In_2O_3's conductivity. It is expected that the surface oxygen desorption process will slow down due to fewer adsorbed oxygen existing on the surface, leading to a slow increase in the photocurrent. The initial fast decrease of photocurrent after turning off the UV LED is the reverse process as that mentioned above. After turning off the UV LED, the oxygen will reabsorb to the surface and capture the electrons from the nanoparticle surfaces, which lead to the reduction of current inside the film. This effect has been studied by Zhang *et al.* who proved that NO_2 can significantly reduce the falling time of In_2O_3 nanoparticles because of its stronger electron capturing effect compared with oxygen [8].

4. Conclusion

In summary, bandpass photodetector with high responsivity in near-UV region was created by depositing PVA-coated In_2O_3 nanoparticles onto epitaxially grown GaN substrates. The gain in the photoconductive mode of In_2O_3 nanoparticles under UV illumination contribute to the high responsivity of the photodetector. Future work will focus on creating visible blind UV photodetectors and improving the response time by improvements on materials and structures.

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