BIO-SENSING SENSITIVITY OF A NANOPARTICLE BASED ULTRAVIOLET PHOTODETECTOR

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Bio-sensing sensitivity of a spectrally selective nanoparticle based ultraviolet (UV) photodetector is characterized in comparison to a silicon photodiode and a photomultiplier tube (PMT). The nanoparticle based photodetector is comprised of poly-vinyl alcohol (PVA) coated zinc-oxide (ZnO) nanoparticles deposited on an aluminum-gallium-nitride (AlGaN) epitaxially grown substrate. The sensitivity was determined by measuring the fluorescence intensity of the native fluorophore, tryptophan, in Escherichia coli (E-coli, ATCC-25922) cells. Tryptophan intrinsically fluoresces with a peak at 340 nm under 280 nm UV light illumination. It is shown that this detector can sense the concentration of E-coli to $2.5 \times 10^8$ cfu/mL while the silicon photodiode cannot detect the intrinsic fluorescence at all. Nevertheless, the PMT outperformed the ZnO nanoparticle-AlGaN substrate based photodetector with the ability to sense E-coli concentrations to $3.91 \times 10^6$ cfu/mL. However, because PMT based systems are commonly limited by high dark current, susceptible to environmental changes, sensitive to ambient light, and have high power consumption, biological detection systems comprised of these ZnO nanoparticle-AlGaN substrate based photodetectors can be more effective for near real time characterization of potential bacterial contamination.

Keywords: bio-sensing; ZnO nanoparticles; AlGaN substrate; tryptophan fluorophore.

1. Introduction

Intrinsic fluorescence spectroscopy has been recognized for use in the non-invasive and near real time assessment of microbial contaminants. However, the majority of spectroscopy systems utilize a photomultiplier tube (PMT) as detectors since PMTs are very sensitive and thus capable of detecting the weak fluorescence signal. Since PMTs commonly have high dark currents, are susceptible to environmental changes, are sensitive to ambient light, and consume high amounts of power, a microbial detection system comprised of another detector type would be advantageous.

Semiconductor based detectors provide an alternative to PMTs. However, many semiconductor materials such as silicon are not ideal for detectors with high responsivity in the ultraviolet (UV) range under room conditions. Therefore, wide band gap material such as zinc-oxide (ZnO), gallium-nitride (GaN), and aluminum-gallium-nitride (AlGaN) are better matched to detect light in the UV range. Still, efficiency and sensitivity of the conversion of incident radiation to current for these bulk materials is limited by high dark current and inefficient light coupling to the active area. Therefore nanoparticles of these
materials are attractive as they take advantage of three dimensional quantum confinement effects that correspond to the continuous tuning of the spectral wavelength and improved device performance\textsuperscript{9}. ZnO nanostructures, in particular, are studied since they are easy to fabricate, can have a large active area, and are relatively low cost\textsuperscript{9-14}.

In this paper a spectrally selective nanoparticle based UV photodetector, fabricated by spin-casting ZnO nanoparticles coated with poly-vinyl alcohol (PVA) onto an AlGaN substrate, is characterized in comparison to a UV enhanced silicon photodiode (Model UV-100 from UDT Sensor Inc.) and a PMT (Model H8249 from Hamamatsu Photonics K.K.). Bio-sensing sensitivity was determined by measuring the intrinsic fluorescence intensity of the native fluorophore tryptophan in various dilutions of \textit{Escherichia coli} (E-coli, ATCC-25922) cells. An explanation for the sensitivity of the ZnO nanoparticle-AlGaN substrate detector is proposed.

2. Background Information

2.1. Principle of Intrinsic Fluorescence Spectroscopy

Intrinsic fluorescence spectroscopy is a quantitative method to monitor cells by exciting intracellular biological molecules with an external light source of a specific wavelength. This stimulation results in an energy yield reaction producing a naturally occurring light emission spectrum of lower energy. Intrinsic fluorescence intensity is proportional to the excitation source’s intensity. It is also proportional to the concentration of biological molecules. This is a non-invasive, reagentless, optical means to detect and characterize biological organisms.

A variety of intracellular biological molecules exhibit intrinsic fluorescence and each of their maximum absorption wavelengths are listed: tryptophan (280 nm excitation), nucleic acids (260/280 nm excitation), NADH (340 nm excitation), FAD (440 nm excitation)\textsuperscript{8}. Of these, it was demonstrated tryptophan can accurately discriminate microorganisms from different taxonomical families by examining wavelengths from 305-400 nm following excitation by 270 nm light\textsuperscript{2}. It is also shown that by exciting tryptophan, tyrosine, phenylalanine, DNA and RNA with a 250 nm light and analyzing the resulting spectra can allow more than 97\% accurate identification at the genus, species, and subspecies level\textsuperscript{4,5}.

Figure 1 shows the fluorescence emission spectrum of tryptophan in E-coli when excited by a 280 nm light. It demonstrates a peak exists at approximately 340 nm. Cell concentration can be extrapolated therefore by measuring the intensity of the fluorescence between 300 nm to 400 nm.

2.2. Nanoparticle based UV Photodetector

A nanoparticle based UV photodetector fabricated and characterized by Qin et al. is tested for its bio-sensing sensitivity\textsuperscript{10}. As depicted in Figure 2a the device structure consists of ZnO nanoparticle coated in PVA spin-casted onto an AlGaN substrate UV
photodetector. UV light which is generated by tryptophan’s fluorescence passes through the AlGaN layers first before reaching the ZnO active material. As depicted in Figure 2b, due to the absorption properties of AlGaN combined with that of the ZnO nanoparticles the light absorbed in the ZnO active layer is limited to between 300 nm and 380 nm, with a responsivity of 304 mA/W at 340nm. The responsivity of the device at 280nm is 2.4 mA/W. Thus, the ZnO nanoparticle-AlGaN substrate device acts as a spectrally selective detector insensitive to the 280nm light needed to produce tryptophan’s fluorescence.

Fig. 1. Fluorescence emission spectrum of Escherichia coli’s (ATCC-25922) fluorophore tryptophan when excited by a 280 nm light. Spectrum is measured using a SPEX Fluorolog Tau-3 spectrophotometer.

Fig. 2. (a) Structure of the ZnO nanoparticle-AlGaN substrate based UV photodetector and (b) band-pass (square: 300-380 nm) responsivity of back illuminated photodetector based ZnO nanoparticles-AlGaN substrate as it relates to the absorption spectra of AlGaN (hollow circle) and ZnO nanoparticles (hollow diamond).
3. Experimental Details

3.1. Biological Sample Preparation

A controlled experimental procedure relative to growth conditions and sample preparation of *Escherichia coli* (E-Coli, ATCC-25922) was used. From the pure E-coli cultures samples were grown in Bacto Tryptic Soy Broth (manufactured by BD Worldwide) at 30°C for 16 to 18 hours in an incubator shaker which is set to 150 rpm. Several colonies were harvested and suspended in a small volume of phosphate-buffer-saline (PBS) solution. The PBS solution was removed by centrifugation at 4400 rcf for 10 min. Then, cells were washed with the PBS solution and centrifuged as described above. Finally, the pellet was suspended in a defined volume of PBS solution in order to obtain an optical density $\text{OD}_{400\text{nm}-450\text{nm}} = 0.5$. Optical density (OD) of bacterial cultures was measured using a Klett photoelectric colorimeter. Part of this suspension was removed and placed into a separate tube containing the previously defined volume of PBS solution to create a 1:2 dilution. Subsequent dilutions were made following the last step.

3.2. Optical Setup

A schematic of the biological fluorescence detection setup is shown in Figure 3. It consists of a Sensor Electronics Technology Inc.’s (SET Inc.) 280 nm ball lens UV LED as the excitation source placed 90° to the detector axis. The ball lens focuses the 280 nm beam to a single point. A current of 10.2 mA is applied to the 280 nm UV LED to generate an optical intensity of 158.31 $\mu$W. The emission source (the biological material) is placed inside of Starna Cell quartz fluorometer cuvette with a 3 mm path length, located as shown in Figure 3. A high transmission 280 nm ($\pm 10$ nm) band pass filter (Asahi Spectra Co, Torrance, CA) is placed directly against a custom-made cuvette holder to limit the excitation light to specifically 280 nm. For the silicon photodiode and the PMT a high transmission 340 nm ($\pm 10$ nm) band pass filter (Asahi Spectra Co,
Torrance, CA) is used. A band pass filter was not used with the ZnO/AlGaN nanoparticle detector for its spectral selective properties.

4. Results and Discussion

Figure 4 shows the bio-sensing capability of the UV enhanced silicon photodiode in comparison to the ZnO nanoparticle-AlGaN substrate based detector within the system above. The silicon photodiode was biased at 0V whereas the nanoparticle detector was biased at +20V, the normal applied voltages for these particular detectors. Under the highest concentration of E-coli cells (2 x 10^9 cfu/mL) the silicon photodiode could not detect any signal.

In Figure 5 the bio-sensing sensitivity of the ZnO nanoparticle-AlGaN substrate based photodetector under +20V bias is compared to the PMT. The lowest concentration the ZnO nanoparticle-AlGaN substrate photodetector can detect is 2.5 x 10^8 cfu/mL. The PMT can detect to a concentration of 3.91 x 10^6 cfu/mL. The ZnO nanoparticle-AlGaN substrate photodetector has a greater bio-sensing sensitivity compared to the silicon photodiode due to two reasons: first, it is spectrally selective, and second, it has a higher spectral responsivity. As indicated in Figure 6 the ZnO nanoparticle-AlGaN substrate photodetector is spectrally selective between 300 nm to 380 nm. However, the silicon photodiode (and the PMT) are not. Therefore, to limit the detection region to the intrinsic fluorescence of tryptophan, filters are required. As seen in Figure 7, the Asahi bandpass filter experimented with in this paper absorbed 30% of the transmitted 340nm light, compared to the AlGaN substrate that absorbs no light above 306nm. Transmission losses caused by the filter reduce the signal the detector can obtain, however with better filters the sensitivity of the silicon photodiode and PMT based system will improve. Still, these better filters increase the cost of the overall
device. Also as indicated in Figure 6, the responsivity of the nanoparticle photodetector is greater than that of the silicon photodiode from 335 nm to 380 nm. At 340 nm the responsivity of the ZnO nanoparticle-AlGaN substrate photodetector is 0.304 A/W when the total incident light intensity is 22.32 nW on the active area. This is 1.05 times the UV enhanced silicon photodiode’s responsivity for that region.

Fig. 5. Bio-sensing sensitivity measurements for a PMT (square solid line) and the ZnO nanoparticle-AlGaN substrate photodetector (circle dashed line) with respect to concentrations of *Escherichia coli* (ATCC-25922) (Excited at 280 nm).

Fig. 6. Spectral responsivity of the UV enhanced silicon photodiode (black square) compared with the backilluminated nanoparticle detector (black circle). Spectral sensitivity of a PMT\(^{15}\) (black triangle, taken with permission from Hamamatsu Photonics K.K. H8249 datasheet).
This higher responsivity can be attributed to the process of photoconduction in ZnO nanoparticles. The photoconduction in ZnO nanoparticles originates from the presence of oxygen-related hole-trap states at the nanoparticles’ surface. As Soci et al. explains, the adsorbed oxygen molecules on the ZnO nanoparticles surface will capture free electrons to form chemisorbed oxygen \([\text{O}_2(\text{g}) + e^- \rightarrow \text{O}_2(\text{ad})]\). When illuminated by UV light with the photon energy larger than the band gap energy \(E_g\) of ZnO (\(h\nu > E_g\)), the light generated free carrier concentration increases and holes migrate to the surface. As electrons and holes pair are generated on the surface oxygen-related hole-trap state neutralize the chemisorbed oxygen \([h^+ + \text{O}_2(\text{ad}) \rightarrow \text{O}_2(\text{g})]\). This prevents charge-carrier recombination thus contributing to the higher gain. This process also prolongs the lifetime of the photogenerated carriers\(^{14}\).

### 5. Conclusion

In conclusion, the bio-sensing sensitivity of the ZnO nanoparticle-AlGaN substrate UV photodetector for the detection of the intrinsic fluorescence of tryptophan in *Escherichia coli* (ATCC-25922) is better than a UV enhanced silicon photodiode (which cannot detect any fluorescence), but does not compare to a PMT (which can detect fluorescence at 64 times weaker dilution than the nanoparticle detector). The ZnO nanoparticle-AlGaN substrate UV photodetector has certain advantages for bio-sensing compared to the silicon photodiode and the PMT. It is visible-blind, spectral selective, and has filterless UV detection abilities. Also, as seen in Figure 8, the responsivity of the ZnO nanoparticle-AlGaN substrate detector is greater than that of the silicon photodiode at
340nm by 14mA/W. Therefore, a biological detection system comprised of ZnO nanoparticle-AlGaN substrate based photodetectors can be more effective for near real-time characterization of potential bacterial contamination in a filterless situation.

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