Group III – nitride materials for ultraviolet detection applications

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ABSTRACT

High performance ultraviolet (UV) detectors have been fabricated using group III- nitride materials grown by molecular beam epitaxy (MBE). GaN PIN detectors exhibit near quantum efficiency limited responsivity, sharp spectral cutoff (3 orders of magnitude drop by 400 nm and near 5 orders of magnitude to visible wavelengths), and high shunt resistance of several hundred mega-ohms for 0.5 mm^2 active area devices. Comparison of PIN and Schottky devices is presented. The capabilities of group III-nitride based ultraviolet (UV) detectors is discussed in relation to suitability in ultraviolet sensing applications such as high temperature flame sensing, UV-B solar radiation monitoring, and high intensity UV dosimetry.

Keywords: ultraviolet photodiode, solar-blind photodiode, gallium nitride, flame sensing, UV-B radiometry

1. INTRODUCTION

The group III-nitrides are semiconductor compounds formed from elements (Al, Ga, and In) in the third row of the periodic table with nitrogen. They are a subset of the III-V compound semiconductors which are all formed from elements in rows III and V of the periodic table More familiar III-V semiconductors are GaAs, GaP, and ternary variations such AlGaAs. These materials are used to make the omnipresent red, green, and amber LEDs.[1] Like the established III-V semiconductor material systems, the group III-nitrides are also very efficient optical emitters and detectors. The difference with the nitrides is that their bandgaps fall in the energy range corresponding to blue and ultraviolet. For GaN this is 3.4 eV, corresponding to a wavelength of 365 nm. For comparison, silicon has a bandgap of 1.1 eV, corresponding to 1.1 µm. Because their bandgaps are large, the group III-nitrides are called "wide bandgap" materials.[2] Wide bandgap materials have advantages for optoelectronic and high temperature or high power devices. Because of its wide band gap, GaN based detectors do not respond to long wavelength visible and infrared radiation. This makes them invaluable for UV sensing applications where there is a need to discriminate against a high background of blackbody radiation, such as a combustion process, or solar ultraviolet measurements. Much higher temperatures are required to thermally excite an electron to the conduction band of a wide bandgap material. This means electronic devices can function well at much higher temperatures. MIL spec silicon electronics are limited to less than 125 °C. Group III-nitride transistors have been operated at 425 °C.[3]

A unique characteristic of photodiode detectors based on the III-nitride ternary alloys is the ability to adjust the long wavelength at which the detectors begin to respond by varying the semiconductor band-gap. The band-gap is determined by the material composition. By changing the percentage composition of Al or In, the wavelength at which the devices begin to respond can be shifted shorter and longer relative to GaN. Increasing the aluminum mole fraction in the AlGaN ternary alloy increases the bandgap above that of GaN, while increasing the mole fraction of indium in InGaN ternarys *decreases* the bandgap with respect to GaN. In principle, detectors with long wavelength turn-ons in the range of 200 to ~600 nm can be covered by the two ternary III-nitride systems. In practice the very extremes of this range cannot be reached due to material problems. For example, high aluminum composition AlGaN becomes very resistive, eventually turning into an insulator. The maximum limit of aluminum content which produces material having sufficiently high semiconductor properties for fabrication of photovoltaic detectors is still being

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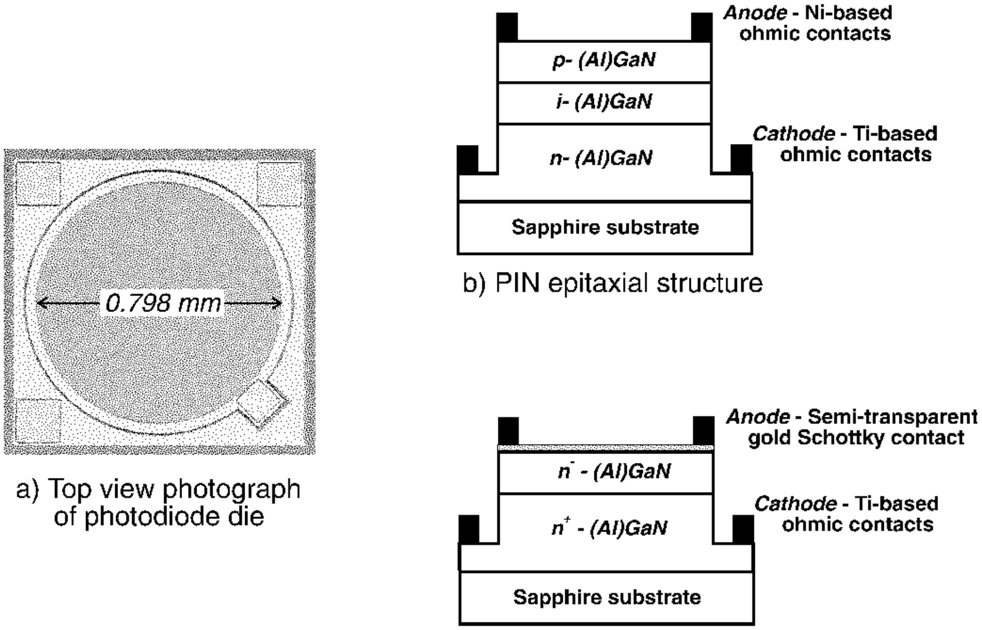
tested. In this work we demonstrate an AlGaN Schottky photodiode having peak response at 250 nm, the shortest III-nitride photovoltaic device demonstrated to date. This device corresponds to a material composition of 56% aluminum.

2. III-NITRIDE MATERIAL GROWTH BY MOLECULAR BEAM EPITAXY

In this work the GaN and AlGaN epi-layers for the photodiodes were deposited by molecular beam epitaxy (MBE). MBE is an extremely versatile technique for growing semiconductor compounds and multilayer structures. In MBE various atomic and molecular fluxes are generated by heating the materials in special ovens called effusion cells in an ultrahigh vacuum chamber (base pressure $< 5\times10^{-11}$ torr). These fluxes converge on a heated substrate to form thin films of desired materials. For this work c-plane sapphire is used as the substrate. Effusion cells are used for the group III elements, aluminum, gallium, and indium, and for the n- and p-type dopants, silicon for n-type material and magnesium for p-type. The group V element, nitrogen, requires a specialized source to create activated nitrogen. An RF plasma source is used to provide nitrogen atom for the growth of group-III nitrides. N_2 is too thermodynamically stable to react with Ga, but the atomic nitrogen species formed in the plasma react readily with group-III metals to form nitride films. The basic concept of this source is to create a plasma in high purity N_2 through an inductively coupled RF field. RF energy (200 to 550 W) is fed into the source through a water cooled copper coil. A pyrolitic boron nitride (PBN) tube with a changeable nozzle is centered between the RF coils. Nitrogen is introduced to the tube and a plasma is created within it.

3. PHOTODIODE FABRICATION

The results presented in this paper are for both PIN and semi-transparent metal Schottky photodiodes. The fabrication of GaN photodiodes grown by MBE has been previously described.[4] In this work, individual detectors are 0.5 mm^2 active area devices that look like the one shown in part a of Figure 1. The epitaxial structure of PIN photodiodes is illustrated by part b of Figure 1. It consists of a 1 to 2 μm *n*-(Al)GaN buffer layer doped at $\sim5\times10^{18}$ cm^{-3} followed by an *i*-(Al)GaN region unintentionally n-type doped at $\sim1\times10^{16}$ cm^{-3} with a thickness of 5000 Å and a topmost 1000Å *p*-(Al)GaN layer Mg-doped p-type at $\sim1\times10^{18}$ cm^{-3}. A schematic cross section of the semi-transparent metal Schottky structure is shown in part c of Figure 1. It has the same n+ buffer layer as in a *PIN*. The active, absorbing region is intentionally doped to $\sim8 \times 10^{16}$ cm^{-3}. A semi-transparent Schottky metal is used to create the junction on this layer. For this work the Schottky contact was formed from ~100 Å of gold.



a) Top view photograph of photodiode die

b) PIN epitaxial structure

c) Semi-transparent Schottky epitaxial structure

Figure 1. a) A photodiode die consists of a circular mesa having an optically active area of 0.5 mm^2, b) schematic cross section of a PIN structure, c) schematic cross section of a semi-transparent metal Schottky device.

4. PERFORMANCE CHARACTERIZATION OF III-N PHOTODIODES

Both PN[3,5,6,7,8,9,10] and Schottky junction[11,12,13,14] (Al)GaN photodiodes having high quantum efficiency responsivity and low dark current leakage have been reported in the literature. In this section the III-nitride photodetectors fabricated for this work are characterized for their spectral responsivity and electrical performance.

4.1 Spectral Responsivity

The spectral responsivities for the GaN PIN and the AlGaN semi-transparent metal Schottky photodiodes are shown in Figures 2 and 3 versus wavelength and photon energy, respectively. These figures illustrate devices ranging in aluminum composition from 0% aluminum in the binary GaN to 56% aluminum in an AlGaN ternary compound. As the aluminum composition increases, the responsivity wavelength is moved deeper into the UV. GaN devices exhibit significant responsivity for wavelengths shorter than 365 nm; for 56% AlGaN, significant responsivity is shifted to wavelengths shorter than 250 nm. By tailoring the composition of the semiconductor, III-nitride photodiodes can be "tuned" to respond in different wavelength ranges.

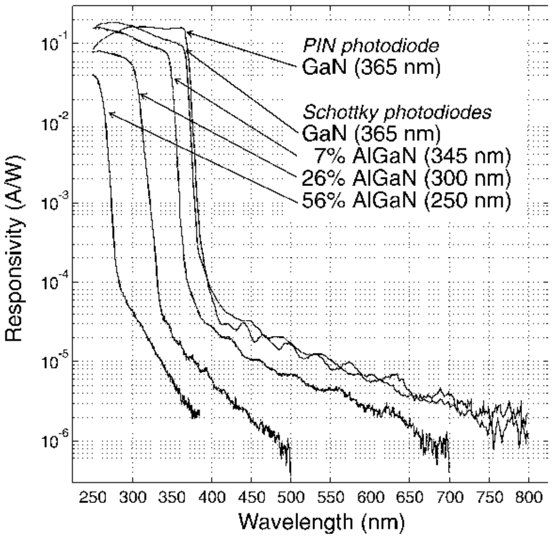


Figure 2. GaN and AlGaN photodiode spectral responsivities as a function of wavelength.

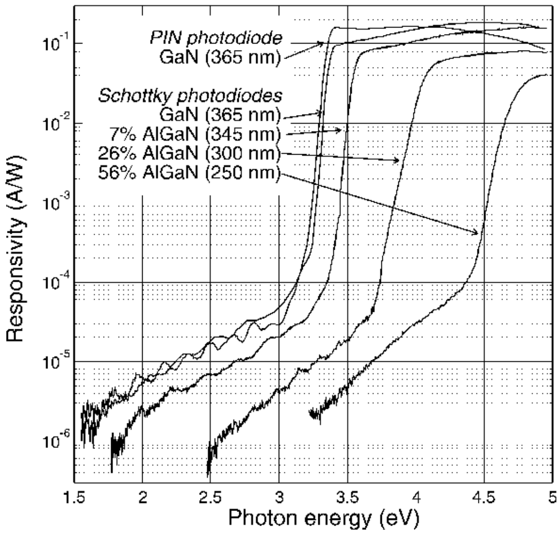


Figure 3. III-nitride photodiode spectral responsivities plotted versus photon energy.

The responsivity of the PIN and Schottky photodiodes follows the absorption of light in the depletion regions of the devices. For the PIN structure the active absorption regions are primarily the upper p-layer and the unintentionally doped, intrinsic layer. For the semi-transparent metal Schottky photodiodes it is in the depletion region created at the metal-semiconductor interface. The absorption coefficient of direct bandgap semiconductors follows a square root dependence on photon energy in excess of the energy gap, Equation 1.[15]

$$\alpha = A(h\nu - E_g)^{1/2} \qquad \text{for } h\nu > E_g \qquad \text{Equation 1.}$$

The absorption coefficient, A, for GaN is ~7 x 10^4 cm^{-1}.[16] This approximation to the absorption coefficient is valid for photon energies above the bandgap to 6 eV, or ~200 nm. At higher energies, more structure appears in the GaN dielectric function than can be described by a simple model.[16]

The spectral responsivities of the III-nitride photodiode devices shown in Figures 2 and 3 exhibit similar characteristics: 1) a slowly varying, and usually increasing, response at wavelengths shorter than the semiconductor bandgap, 2) an exponential decrease in responsivity in the bandtail region just below the bandgap (i.e. longer wavelengths), and 3) a slow, exponential decrease in responsivity at wavelengths significantly longer than the bandgap.

III-nitride photodiode responsivity above the bandgap generally follows the square root dependence of absorption given in Equation 1. The absorption in the depletion region increases with shorter wavelength light, generating more carriers and a higher photocurrent. For the Schottky devices with no applied bias, the depletion extends from the metal interface to a depth determined by the semiconductor doping level. The depth of this depletion region can be increased by reverse biasing the Schottky junction. An increased depletion region increases the absorption pathlength, and likewise increases the photocurrent. Figure 4 illustrates this point by showing the spectral response of a 26% AlGaN Schottky photodiode in photovoltaic mode and with 1.5 volts reverse bias. The above bandgap responsivity increases by ~30% with the applied bias.

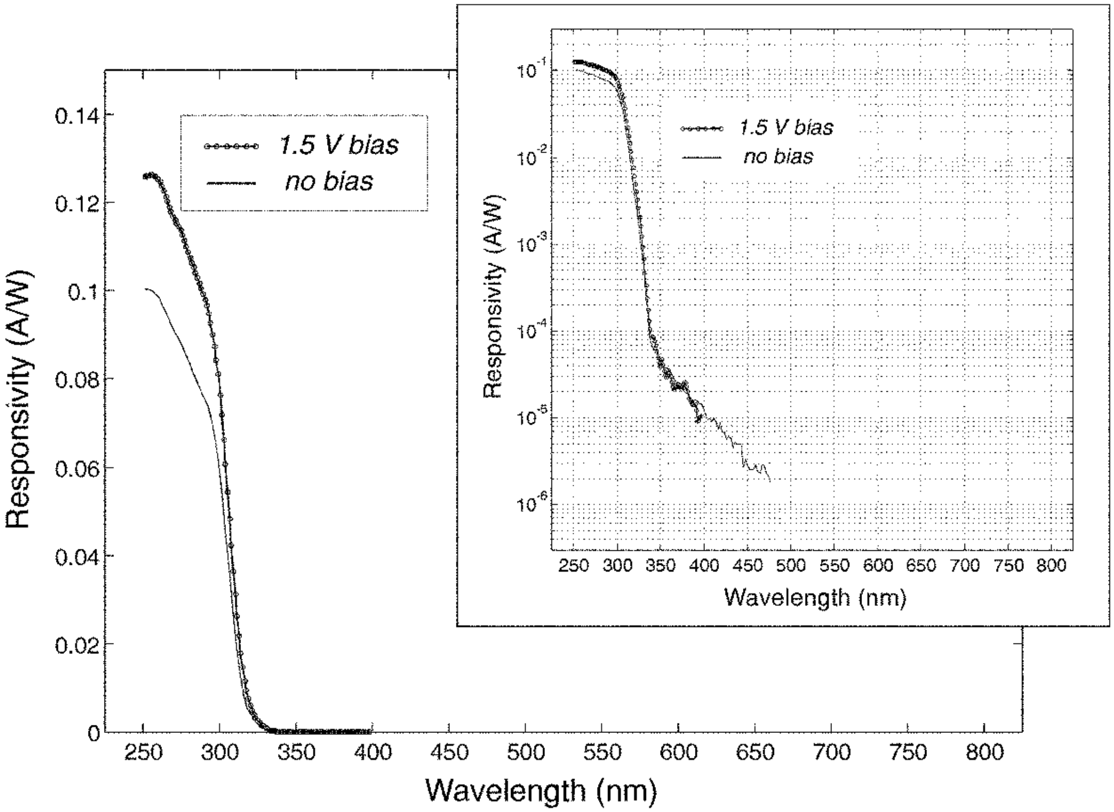


Figure 4. Responsivity of 26% AlGaN Schottky photodiode in photovoltaic mode and at 1.5 volts reverse bias.

For the GaN PIN photodiodes the absorption region is primarily in the undoped, intrinsic region and the topside p-GaN layer. The photovoltaic responsivity of the GaN PIN from the bandgap to ~300 nm is higher and flatter than for the comparable GaN Schottky. The greater absorption length achieved with the i-region ensures that practically all light is absorbed in the active region of the device. But at wavelengths shorter than ~300 nm the responsivity of the GaN PIN begins to decrease. This is due to the strong absorption of short wavelength light in the p-type upper layer. P-type GaN material is very resistive. Electron-hole pairs made near the surface recombine before they are separated at the depletion region. Shorter wavelengths are more strongly absorbed and are therefore more strongly attenuated.

For all the photodiodes presented here, an exponential decrease in responsivity is observed for photon energies just below the bandgap. This behavior is typical for direct bandgap semiconductors. The steepness of this slope is determined by transitions between bandtails and is a factor of doping levels and the overall quality of the material. The exponential falloff is ~2x slower for the 56% aluminum content photodiode in comparison to GaN. For the GaN PIN and Schottky photodiodes the responsivity in mid-transition falls by 1/e in 0.023 eV, corresponding to a 10x decrease in ~6 nm. For the 56% AlGaN Schottky, the 1/e fall occurs in 0.049 eV, or a decade fall in ~8 nm.

Since all AlGaN alloys form direct bandgap semiconductors, there should be no absorption at wavelengths longer than the bandgap, and hence no long wavelength responsivity. However, all of the devices show a small but measurable response at wavelengths much longer than the bandgap. This sub-bandgap response also falls exponentially, but at a much slower rate than for the bandtail transitions. Small oscillations in responsivity at long wavelengths are seen in all the devices, and are particularly noticeable for the GaN PIN. These are thin film interference oscillations between the air-(Al)GaN and sapphire-(Al)GaN interfaces. The experimental setup used for the spectral responsivity measurements limits detection of responsivity to ~1 x 10^{-6} A/W. However, using a bright, HeNe laser, it is possible to make point measurements of responsivity at 632 nm. Measurement of an AlGaN device responsivity at this wavelength agrees well with that predicted by extrapolating the exponential fall off observed closer to the bandgap. While sub-bandgap response has been reported previously in the III-nitrides, a detailed explanation to its origin has not yet been presented.

4.2 Electrical Characteristics

The IV characteristics of the GaN PIN and 26% AlGaN Schottky photodiodes are shown in Figure 5. The Schottky diode turns on at ~1.1 V; the GaN PIN at ~3.2 V. Both types of devices exhibit soft breakdown in reverse bias. The dark current leakage at 10 mV reverse bias is on the order of a few picoamps corresponding to a shunt resistance is greater than 1 GΩ.

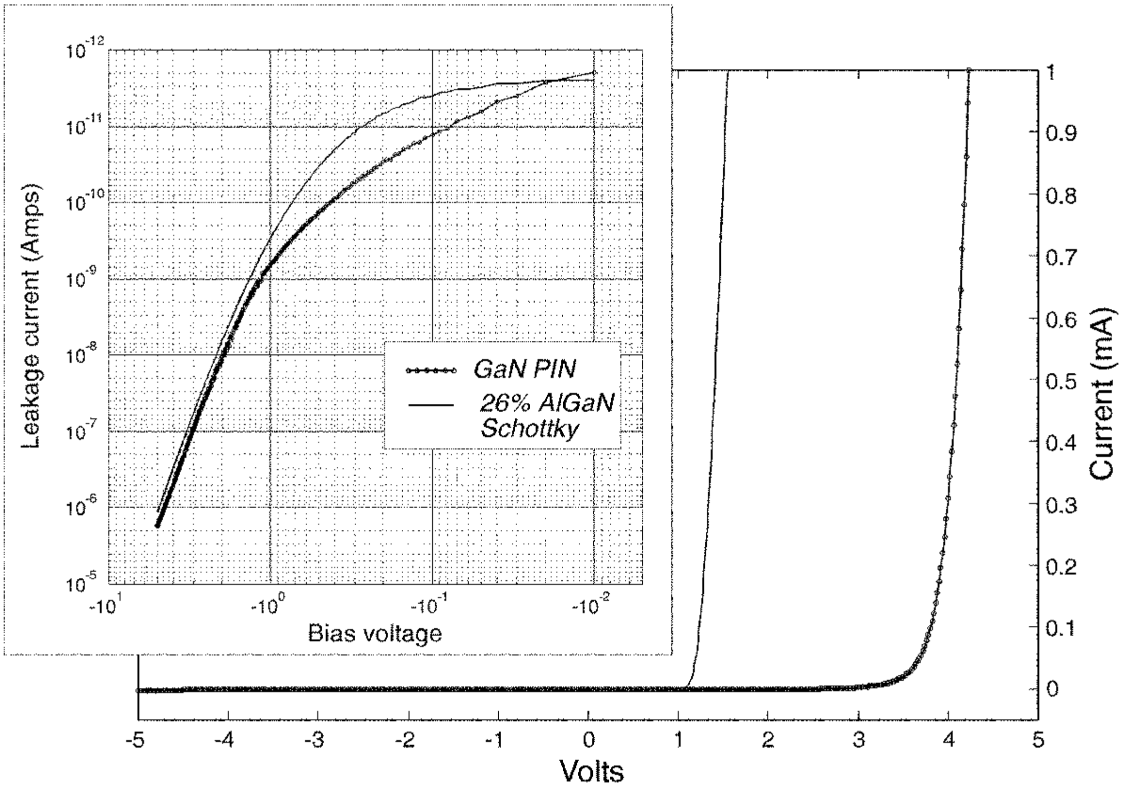


Figure 5. IV characteristic of a GaN PIN and a 26% aluminum AlGaN Schottky photodiode. The inset shows the reverse bias dark current on a log scale.

The dark current IV and the IV under ~300 μW of UV irradiation for an AlGaN Schottky is shown in Figure 6. The increasing photocurrent with revrse bias is due to the widening of the depletion depth.

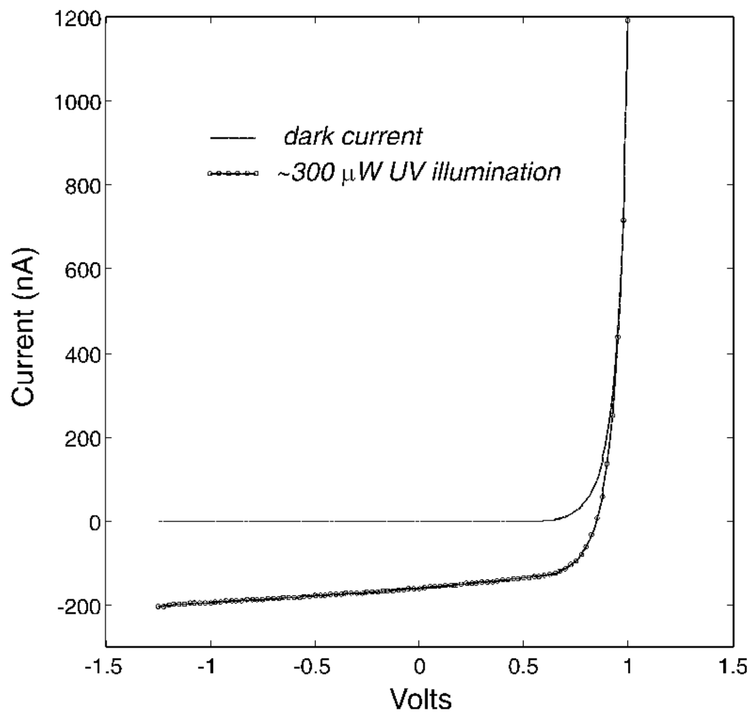


Figure 6. IV characteristic of an AlGaN Schottky photodiode in the dark and under ~300 μW of UV irradiation below the turn on wavelength.

5. ULTRAVIOLET SENSING APPLICATIONS OF III-N PHOTODIODES

5.1 Combustion monitoring

Group III-nitride photodetectors made from aluminum gallium nitride (AlGaN) are ideally suited for ultraviolet combustion sensing. Ultraviolet flame sensing has application in industrial combustion processes such as for turbine engines used in power generation or for natural gas or other hydrocarbon burning furnaces and boilers. Because the turn-on wavelength of an ultraviolet detector made from the group III-nitride material aluminum gallium nitride (AlGaN) can be "tuned" by adjusting the percentage of aluminum in the composition, these devices can be optimized for specific flame sensing applications. For example, solar-blind combustion sensing, an essential requirement for safety conscious applications such as detection of afterburner ignition on military jet aircraft, is possible with group-III nitride materials. The 56% aluminum AlGaN Schottky photodiode has its peak responsivity at 250 nm, and falls 10^3 in response by 300 nm, making the device "blind" to solar radiation penetrating the earth's atmosphere. Figure 7 shows the terrestrial solar irradiance and UV/visible flame emission from JP-4 jet fuel. These spectra have been normalized to their maximum values to illustrate the orders of magnitude reductionvariation in output power from the visible to the ultraviolet. To discriminate the ultraviolet emission of a combustion flame from the blackbody background requires an extremely sensitive detector with 10^6-10^7 rejection of visible and IR radiation. The normalized spectral responsivities of the 56% aluminum AlGaN Schottky photodiode and a SiC p*n* junction photodiode are also shown in Figure 7.

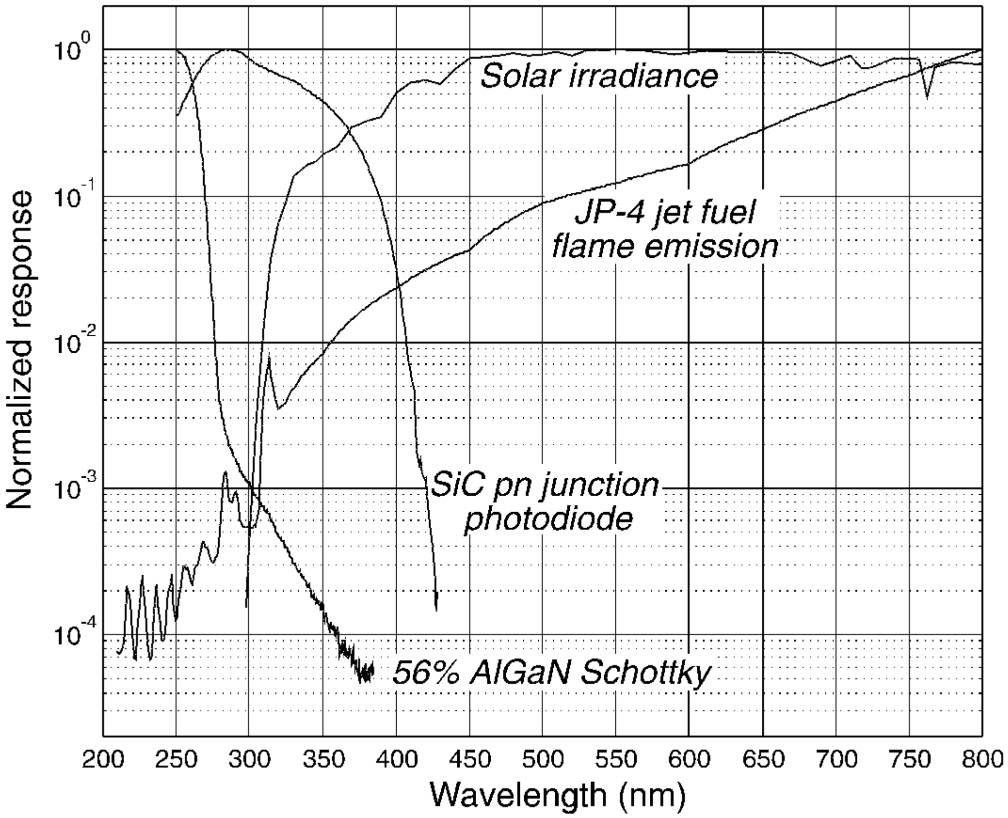


Figure 7. Solar irradiance at the earth's surface and the UV/visible emission from jet fuel combustion are shown in comparison with the spectral responsivity of a solar blind AlGaN Schottky photodiode and a SiC *pn* junction photodiode. All the curves have been normalized to their maxima in this wavelength range.

Silicon carbide is a competing wide band gap material technology for solid state UV combustion sensing technologies. While GaN and SiC have many similar material properties such as thermal conductivity, thermal stability, breakdown fields, and band gap, GaN has superior optoelectronic properties. SiC is an indirect band gap material, whereas GaN is direct. SiC cannot be alloyed with other elements to tailor the band gap as GaN can be with aluminum and indium. The peak responsivity of SiC is near 280 nm, making it comparable to AlGaN devices, but adjustments of the spectral responsivity range to suit specific needs as is possible with AlGaN, cannot be achieved with SiC. And, as an indirect bandgap semiconductor, it does not have the sharp, bandedge cutoff like the III-nitride materials. It has substantial responsivity at solar wavelengths, as shown in Figure 7. SiC does have an advantage over III-nitride materials in that SiC bulk wafers are available for homoepitaxial growth. The low defect density in SiC p-n junctions grown on SiC substrates have superior electrical properties (*e.g.* high shunt resistance, low reverse bias leakage) to the current state of the art III-nitride material grown heteroepitaxially on sapphire. But superior heteroepitaxial growth techniques for the III-nitrides are developing at a rapid pace, and it is likely that electrical properties of III-nitride photodetectors will soon match those of SiC.

5.2 UV-B solar irradiance monitoring

The effectiveness ultraviolet radiation in causing sunburn is strongly dependent on wavelength. The weighting factor for sunburning effectiveness is known as the erythemal action spectrum, or EAS. An international standard for EAS has been defined. It is shown in Figure 8 along with the standard solar irradiance in the same wavelength range. The EAS is at its maximum for wavelengths of 298 nm and less. It falls exponentially for longer UV wavelengths. The EAS at 330 nm is 10^{-3} that at 300 nm. At 400 nm it is 10^{-4} of its maximum value. While the EAS is a sharply decreasing function with increasinglonger UV-B wavelengths, solar irradiance is steeply increasing in the same range. Furthermore, solar UV-B radiation is strongly influences by climatic variations. Ozone absorption is strong in this range. A UV-B sensor designed to measure the effective sunburning dose must closely adhere to the EAS spectrum because small variations in responsivity can cause large discrepancies in calculated dose.

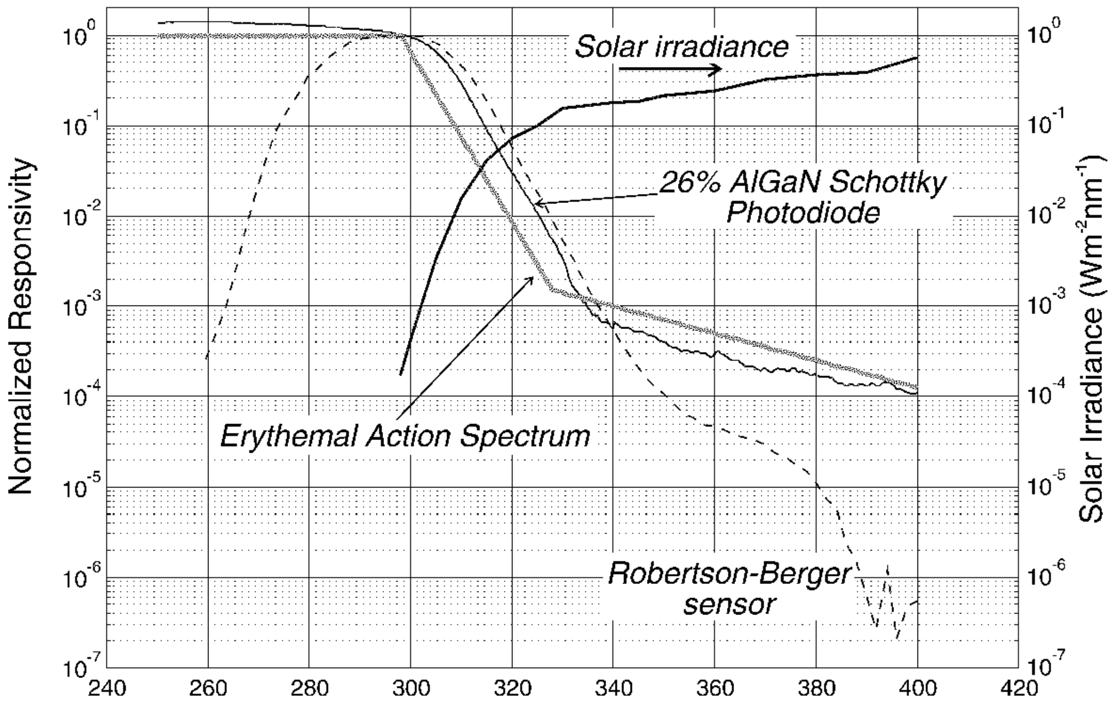


Figure 8. Comparison of 26% aluminum AlGaN Schottky photodiode and Robertson-Berger sensor as approximations to the erythemal response function. Also shown is the solar irradiance in the UV-B band.

The standard for broadband UV-B radiometric instrumentation originated in the late1950's in Australia as part of a proposal to correlate incidence of skin cancer with sunburning ultraviolet dose. A technique for measuring UV-B radiation weighted by a factor resembling the erythemal response spectrum was developed by D. Robertson and later advanced in the United States by D. S. Berger as part of the US Department of Transportation's Climatic Impact Assessment Program. The technique by which these sensors work utilizes a magnesium tungstate phosphor combined with colored glass pre- and post-filters and a photodetector. This sensor design was chosen because it has an action spectrum that is close to, although not an exact match, of the standard erythemal response. AlGaN photodiode technology can be tailored to provide a much closer match to the standard erythemal response. Figure 8 shows the normalized response for a standard Robertson-Berger sensor and for the 26% aluminum Schottky photodiode. The III-nitride photodiode has not been optimized to match the EAS, but as it stands, it is already a closer match than the standard Robertson-Berger sensor.

6. CONCLUSIONS AND FUTURE WORK

GaN and AlGaN photodiodes with aluminum compositions up to 56% have been have been fabricated. Spectral responsivity and electrical properties have been characterized. These devices show high quantum efficiency response in the UV and good rejection of long wavelength visible and IR radiation. Typical shunt resistances for 0.5 mm^2 devices are on the order of a few GΩ. Soft, breakdown is observed at higher reverse bias voltages. Applications for these photodetectors in UV flame sensing, solar ultraviolet radiometry, and high intensity, UV dosimetry are presented. The 56% aluminum AlGaN Schottky photodiode having a photovoltaic responsivity of 0.04 A/W at 250 nm and 10^3 rejection by 300 nm is a true, solar blind, solid-state photodetector, and essential requirement for many flame sensing applications. The 26% aluminum AlGaN Schottky is already a good approximation to the erythemal action spectrum, and, with some additional composition tailoring, an exact match to the EAS should be possible. The III-nitrides are robust, stable materials which are well suited for power and dose measurements with high intensity UV sources. The incorporation of short wavelength AlGaN filters to create robust bandpass detectors make these materials even more valuable for high intensity applications.

While the current work already demonstrates high quality III-nitride devices with unique optical detection properties, future improvements will extend the capabilities of this photodetection technology. The short wavelength limit for photovoltaic AlGaN detectors has not yet been reached. As material growth techniques continue to improve, even shorter wavelength devices will be possible. Improvements in material quality will also lead to increased responsivity, greater out-of-band rejection, and lower dark current leakage.

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