Innovative Development and Prospects of Solar-Blind Photodetectors

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Abstract. This study delves into the advancements and challenges in the development of solar-blind photodetectors, focusing on ultrawide bandgap (UWBG) semiconductors. Solar-blind photodetectors, which operate in the UV-C range shielded by the Earth's ozone layer, are distinguished for their accuracy and reliability in various applications, including aerospace, military, environmental monitoring, and more. The research highlights the significance of materials like AlGaN, diamond, and few-layer hexagonal boron nitride (h-BN) for their exceptional properties such as high responsivity, thermal stability, and immunity to visible light interference. Innovations such as the low-temperature direct growth method for h-BN on sapphire substrates are underscored for enhancing fabrication efficiency and integration prospects. Moreover, the challenges related to doping, epitaxial growth, and substrate optimization are discussed, with insights into potential solutions that could advance the performance and reliability of these detectors. The future of solar-blind photodetection technology appears promising with ongoing efforts to explore new semiconductor materials and enhance device functionalities, ensuring their pivotal role in critical applications across diverse fields.

Keywords: Solar-blind photodetectors; ultrawide bandgap semiconductors; AlGaN; Diamond UV detectors; Few-layer hexagonal boron nitride.

1. Introduction

Solar-blind photodetectors are a specific category of ultrawide bandgap (UWBG) semiconductors, with bandgaps significantly larger than traditional semiconductors. This bit of the spectrum is super interesting because it sits below what the Earth's ozone layer absorbs. Basically, the ozone layer acts like a big sunblock, soaking up most of the sunlight in the UV-C range, which is between 100 to 280 nm. This means that solar-blind detectors, by zeroing in on this UV-C range, don't get messed up by sunlight. So, even when the sun is blazing away, these detectors can spot UV light sources hanging around on the Earth's surface or in the atmosphere, making them incredibly accurate and reliable for certain tasks.

Ultra-wide bandgap (UWBG) semiconductors are quite attractive for solar blind imaging or sensing applications in the deep ultraviolet ($\lambda < 290$ nm) band [1]. These materials inherently absorb only deep UV radiation due to their large bandgap, thus blocking visible light by several orders of magnitude, thus reducing the need for external filters. In addition, UWBG devices are radiation-resistant, lightweight, and do not require cooling to reduce dark current, making them very promising for efficient and compact solar-blind imaging. However, in the growing UV sensor market, detectors based on UWBG semiconductors are hardly present in actual systems and imagers employing UV sensing technology. It is important to note, however, that "UV sensors" also include detectors that operate in the UVA and UVB environments in the wavelength range of 290-400 nm; while Gallium Nitride (AlGaN) and Indium Nitride (InGaN) detectors with appropriate alloy compositions can detect UV radiation in this range, they are not strictly solar-blind UV detectors. The discussion in this report will be limited to solar blind UV detection, which is where UWBG materials and their heterostructures have much to offer.

This type of detector can be used in different fields, from aerospace, and missile warning to biomedical and industrial detection, and since no external filter is needed to block the visible part, the detector can be lighter, thinner, and more stable, and can work better in harsh and extreme environments. However, compared to other fields, the development of this method is still at the R&D

and testing stage, and there is no unified standard for the performance testing of different types of detectors and no engineering solutions on the ground, so it is extremely useful to conduct a preliminary review and discussion of the development of this type of detectors.

2. Working Mechanism of Solar-Blind Photodetectors

Solar-blind photodetector is a term commonly used to refer to devices that do not respond to infrared, visible, or near-UV light but have a high sensitivity to ultraviolet light in wavelengths below about 300 nm. Be advised that on the Earth, solar radiation extends just a bit into the ultraviolet region; the content of UV is immensely higher outside the atmosphere. This, therefore, enables solar-blind detectors to show some response when illuminated with solar light in space. Similarly, one might define the so-called visible-blind photodetectors, whose long-wavelength cut-off is situated close to the range of visibility, e.g., at about 360 nm.

There are, in theory, a great many photodetectors—silicon photodiodes, which can be made solar-blind by adding an optical filter and hence allow the transmission of ultraviolet light while excluding visible light. In practice, however, the term is used mainly for the detectors that are naturally insensitive to visible light and hence do not have a filter for visible light. The solution of this standard is to use the internal photoelectric effect in a semiconductor material with a very wide bandgap. That is, the light emitted, and a much wider range of light cannot be absorbed and would not give rise to photocurrents. In the same way, the effect is also called the external photoelectric effect and could be utilized with materials of quite a large work function. Using any of the two, the responsivity of the visible spectral region could be weaker by orders of magnitude compared with the ultraviolet region. This is not to say, however, that at sufficiently high optical intensities (which are quite feasible for ultrashort pulses), substantial response from longer-wavelength light cannot be observed by two-photon absorption.

The high photon energies of short-wavelength UV light led to rapid degradation of many materials. Solar-blind detectors should be optimized such that they can tolerate UV irradiation with a substantial lifetime dose. Many applications expose them also to large quantities of short-wavelength radiation, which they are to resist. Solar-blind detectors may generally be operated at significantly high temperatures without generating substantial dark currents. Such behavior results from the fact that the energy of the bandgap or the work function is relatively high and thus it suppresses thermal excitations. This behavior can also be useful in those applications in which relatively high temperatures are desirable to avoid the undesirable deposition of some substances. Some of these detectors can be used even for the production of focal plane arrays in UV imaging devices and for some solar-blind cameras (e.g., "AlGaN-based").

3. Different Types of Solar-Blind Photodetectors

3.1. AlGaN-Based UV Detectors

Aluminum Gallium Nitride (AlGaN)-based ultraviolet (UV) detectors have garnered substantial interest for their pivotal applications in environmental, industrial, military, and biological fields. The advantage is that it uses AlGaN-based materials that make it tunable to wide-band gaps, which permit intrinsic detection across the UV band from near-UV to deep-UV regions, including the terrestrial solar-blind region. These characteristics particularly make solar-blind UV detectors important since they will be able to operate without false alarms or be less effective by the sun, a condition that is highly vital for applications like early missile warning systems, environmental monitoring, and non-line-of-sight communications [2].

The growth and epitaxial material techniques and device engineering have enabled tremendous development in AlGaN-based UV photodetectors (PDs) and focal plane arrays (FPAs) over the last decade. The aluminum content variations in AlGaN alloys allow the filling of the whole UV spectrum and provide a precise match of the spectral response of the detector. As a result, high-precision UV detection has been materialized with the developed high-quality AlGaN material together with epitaxial growth, doping, and device fabrication despite the inherent challenge.

3.1.1 Properties

The mainly solar-blind photodetectors using AlGaN have a cut-off response lower than 280 nm. AlGaN-based UV detectors have been praiseworthy because of their high responsivity, thermal stability, and radiation hardness which makes them robust, and fast response speed, all achieved through the wide bandgap properties of the AlGaN materials. Such sensors exhibit good performance in the UV region, down to solar blind, where devices are insensitive to visible and longer-wavelength UV light.

Figure 1 below shows the relationship between cutoff wavelength (bandgap energy) and Al content in AlGaN. According to the data shown, the composition of Aluminum in (Al, Ga) N-based materials indicates that it is more than 40% that can reach the requirements of being insensitive to solar light, which is fundamentally related to the bandgap energy of the AlGaN compound semiconductor. Detection of the regime of operation should be smaller than 280 nm in wavelength and insensitive to longer ones. The bandgap of AlGaN should be more than 280 nm for alloying with a high proportion of Al, which eventually increases the AlGaN bandgap. The amount of Al content higher than 40% in Al guarantees that the photodetector-sensitive layer will have its bandgap large enough for the photodetector to be sensitive only in the UV-C range, hence solar-blind.

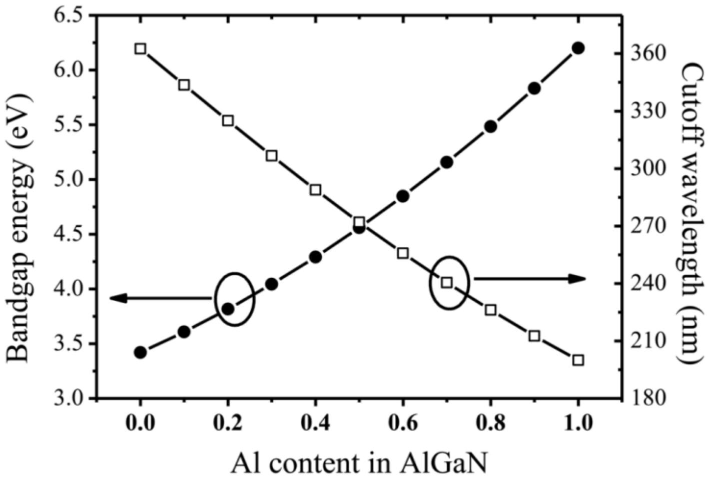

Fig. 1 Bandgap and cutoff wavelength of AlGaN dependent on the Al mole fraction [3].

Epitaxial growth of AlGaN from the 1990s had been optimized for all aspects of its processing, with great attention to metal-organic chemical vapor deposition (MOCVD) growth, and subsequent development and characterization of the deep-UV photodet. Since native AlGaN substrates do not exist, these epi-layers are therefore grown hetero-epitaxially, commonly on a sapphire substrate. Several other substrate materials exist that may be grown on silicon, such as aluminum nitride (AlN) bulk crystals and silicon carbide (SiC) [4-7].

The p-type conductivity in alloys with AlGaN compounds is of special difficulty, as the magnesium (Mg) used in it is characterized by an elevated value of ionization energy. Few doping efficiencies are very direct, but they are affected by this elevated energy of ionization. In the beginning, it would require a huge amount of thermal energy to pull an electron out of the atom of Mg, which should produce a hole participating in the electrical conductivity. With an increase in the ratio of aluminum in AlGaN and a proportion of increments in the bandgap broadening, correspondingly, an increase in the ionization energy of Mg is also reported. Further, it complicates the problem of activating the Mg acceptors and reduces the concentration available for free holes at room temperature, limiting p-type conduction.

Several strategies have been developed to mitigate the challenges posed by Mg's high ionization energy in AlGaN. The typical way of carrying out post-growth annealing, as has been practiced in the industry, is through annealing the doped material at high temperature, giving activation to more

Mg acceptors by ionization and diffusion of these Mg atoms to jump into the lattice. The process aims at increasing the free hole concentration, which will also increase the material's p-type conductivity.

Also, if the AlGaN is delta-doped, then the introduction of Mg at definite layers within the AlGaN structure could result in localized hotter spots of Mg concentration. This may bring about a balanced view, rather than maximizing the opportunity for acceptor activation and hence increasing the chance for better conductivity overall. Alternatively, superlattice structures of AlGaN/GaN or AlGaN/AlN provide an alternate approach to solving the ionization difficulty. Such structures can change the inner electric field and band structure of the semiconductor in such a manner that the impurity ionization of Mg acceptors becomes extremely convenient, hence highly effective p-type doping will result. Supervision can thus achieve higher hole concentrations and mobility more effectively than conventional doping methods. It may also be applied for co-doping with elements, such as oxygen [8].

3.1.2 Performance

The epitaxial layer growth must be developed with the feedback of the device to establish the critical link between growth conditions, structural attributes, and device performance. This is essential in the development of the relationship required to understand, assess, and improve the state of UWBG deep-UV technology. For a comprehensive evaluation of solar-blind photodetectors, it's crucial to consider a range of device parameters including responsivity, external quantum efficiency (EQE), the ratio of photo-to-dark current, UV-to-visible rejection ratio, noise equivalent power (NEP), specific detectivity, dynamic linearity, and 3-dB bandwidth or transient response. The significance of these metrics varies depending on the application. For example, in deep-UV imaging of celestial bodies, the detector's speed or bandwidth might not be as critical since the detector could be waiting extended periods to capture a single photon. However, for some astronomical applications, a rapid response to deep UV light can be crucial. Regardless, these detectors must exhibit extreme sensitivity, exceptional visible light rejection, and superior noise performance. Conversely, for applications like missile plume detection in the UV spectrum, the detector's speed, in addition to its sensitivity, becomes paramount [9].

Considering noise performance, transient speed, and dark current, a comprehensive figure of merit (CFOM) may be introduced:

$$FOM = \frac{G^2}{\tau_{av}\sqrt{I_D}} = \gamma \tag{1}$$

G represents the EQE and τ_{av} is the harmonic mean of the rise time and the fall time as reported in transient measurements [9]. For different devices, I_D depends on various factors, from Schottky, p-i-n diodes to MSM detectors.

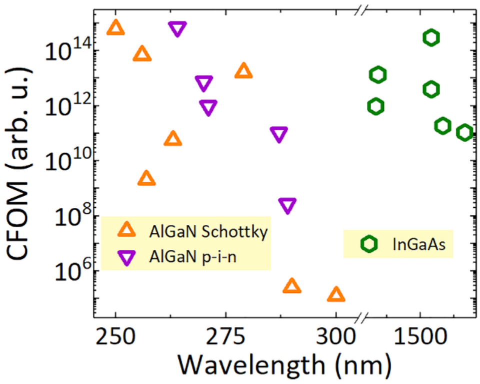

Fig. 2 Scatter plot of the proposed CFOM corresponding to published data points along with a few points from commercially available InGaAs infra-red detectors [9].

The state-of-the-art AlGaN deep-UV photodetectors presented in Figure 3 confirm that their device performance parameters are close to or better than those of traditionally applied very successful InGaAs near-IR detectors. Fundamental and practical barriers that otherwise limit the effectiveness of the AlGaN photodetector, especially in the p-i-n and Schottky configurations, for deep-UV detection or imaging applications, have little bearing on its operation or use when devices yield and exceed the performance benchmarks. Further efforts would be required to conduct a more rigorous investigation concerning the reliability and degradation mechanisms of AlGaN detectors at this juncture of their development, but much could be asserted that basic performance metrics, e.g., bandwidth, EQE, noise, etc., are by no means the showstoppers of their wide-based usage in practical applications [9].

3.2. Gallium Oxide-Based UV Detectors

Ultraviolet photoelectric detection technology has been playing a crucial role in many fields, such as flame sensing, environmental monitoring, missile tracking, and so on. Day-blind light refers to light whose wavelength is less than 280nm, due to atmospheric ozone, oxygen, and other components of the deep ultraviolet light absorption and scattering effect is strong, the radiation on the ground from the sun's day-blind light band of light is almost non-existent. Day-blind UV photodetectors work in the range of day-blind light bands, which can effectively exclude the interference of natural background light and improve the accuracy and efficiency of the detection of radiation from artificial light sources. Most commercially available day-blind UV photodetectors are huge and fragile photomultiplier tubes that require an external power supply to operate. Wide-bandwidth semiconductors (WBG) have high radiation intensity and intrinsic day-blind spectral selectivity. Thus, wide-bandwidth day-blind photodetectors are expected to replace photomultiplier's place in day-blind photodetection. The bandwidth of gallium oxide is usually in the range of 4.4 to 5.1eV, corresponding to the absorption cut-off wavelength of about 250 to 280nm, and has advantages over other wide-bandwidth semiconductors, such as SiC, in terms of preparation cost, product crystal quality, and so on. Therefore, gallium oxide-based day-blind UV photodetector is one of the main directions of wide-bandwidth day-blind UV photodetector research.

Ga_2O_3 has five isomers, called α, β, γ, ε and δ-Ga_2O_3. Among them, β-Ga_2O_3 is the most stable isomer, with a band gap of 4.7–4.9 eV. The other isomers are metastable. After a sufficiently long time or at a certain temperature, they will be converted into stable β-Ga_2O_3. β-Ga_2O_3 is considered a new kind of transparent conductive oxides. This paper focuses on β-, α- and ε-Ga_2O_3.

3.2.1 β-Ga_2O_3

β-Ga_2O_3 is a monoclinic crystal structure, this structure makes it has a high electron mobility and small carrier effective mass, with great electrical conductivity. Moreover, β-Ga_2O_3 has a high critical electric field strength. For the manufacture of ultra-high-power discrete semiconductor devices and ultraviolet photoelectric detector devices, β-Ga_2O_3 has a greater advantage. β-Ga_2O_3 among the isomers of Ga_2O_3 has the highest stability, other Ga_2O_3 isomers at a temperature that is high enough (1800 ℃) will be converted to β-Ga_2O_3.The preparation methods of β- Ga_2O_3 are well established, and β-Ga_2O_3 is currently the most industrialized isomer of Ga_2O_3. High-quality single crystals can be prepared by melt growth methods such as the direct-drawing method, the floating-zone method, and the edge-limited-film method, which is more efficient than most of the other third-generation semiconductors. β-Ga_2O_3 detectors have been demonstrated to offer high response rate values, excellent visible rejection, and ultra-low dark current, although with the inherent problem of slow transient response which almost all photodetectors on gallium oxide have, in some areas where response speed is not significant, such as astronomical observation, has a huge advantage, and with the further study of β-Ga_2O_3, it is possible to accomplish the balance between transient response and gain. Doping of β-Ga_2O_3 with other elements also opens up a road for energy band engineering.

3.2.2 α-Ga_2O_3

α-Ga_2O_3 has a corundum structure similar to that of sapphire, as well as the largest bandwidth (5.5 eV) among all isomers of gallium oxides. It has been possible to prepare α-Ga_2O_3 with high purity by advanced techniques such as Mist CVD. α-$(Rh,Ga)_{23}$ obtained by doping Rh can be used as the npole of a pn knot, to fabricate high-performance devices based on α-Ga_2O_3 [10]. α-Ga_2O_3 is inexpensive to prepare and has deep potential for development in the field of semiconductor materials.

3.2.3 ε-Ga_2O_3

ε-Ga_2O_3 is the only Ga_2O_3 isomer with ferroelectricity, and its crystal structure is the most controversial at present, which is currently considered to be disordered but with P63mc space group symmetry [11]. ε-Ga_2O_3 can be obtained by the epitaxial growth of the HVPE method on a sapphire substrate, which makes it possible to participate in the competition of day-blind ultraviolet optoelectronic devices through heteroepitaxy [12]. Meanwhile, there are still few studies on ε- Ga_2O_3 compared to β-Ga_2O_3 and α-Ga_2O_3, and scholars must carry out relevant experiments and studies to explore how these emerging polycrystals can be helpful for reality [13].

3.3. Diamond UV Detectors

Diamond UV detectors are special kind of devices used for detecting ultraviolet (UV) radiation with the prime material of diamond for the sensing element. Diamond is one of the crystalline forms in which carbon exists and has atoms crystallized in a lattice crystal structure. It finds application in material science for some special applications of UV detection. Diamond has high carrier mobility and is radiation-hard; its high thermal conductivity makes it a material with excellent properties for use in UV detectors based on diamond.

The regeneration method described in the study effectively reduces surface defects without compromising the lens structure's optical properties, as demonstrated by projection experiments [14]. In this context, various efforts in the past included detectors with new structural designs, such as vertical structures with graphene electrodes and groove-shaped detectors, respectively showing better performance as a result of optimized electric field distribution and enhanced carrier collection. These authors suggested another method of restoring the optical quality of a degrading lens structure based on experimental projection and successfully restored the lens structure by effectively reducing the surface defects without deterioration of optical properties.

The regrown lenses preserve the surface, despite the introduction of nanorods on the diamond by etching with oxygen plasma and retaining this capability of light convergence. This fact has been evident to show the success of the method in preserving the lens structure. This was very vital in the way that ensured that the structures were in a position of regrowing back without offset against the enhanced responsivity of the detector. On the other hand, the two main peaks of response are observed in the UV region of the regrown lens detectors, which is ascribable to the interband response and free exciton response of the diamond.

This phenomenon further extends the detected spectral range of diamond UV detectors to the solar-blind UV region without any compromise in transient response performance. The possibility of using these diamond UV detectors is to provide a high-speed response and an excellent noise figure, such as those required in space-borne deep-UV astronomical imaging. This work sets a landmark in the further development of ultraviolet diamond detectors with extreme efficiency and reliability by using the intrinsic characteristics of diamonds and new regrowth innovations.

3.4. Few-Layer Hexagonal Boron Nitride

Hexagonal boron nitride, a two-dimensional wide-band-gap semiconductor, is highlighted for its intriguing optoelectronic properties and wide-ranging applications in deep ultraviolet optoelectronic and two-dimensional electronic devices. One of the grand challenges in the field is the growth of high-quality h-BN directly on dielectric substrates, usually requiring substrate temperatures far above what is practically available or even a post-annealing process. The study reports a method of direct growth on sapphire substrates at a comparatively low growth temperature of 700 °C to produce high-quality few-layer h-BN by using ammonia (NH_3) in the growth chamber during the ion beam sputtering deposition process [15]. This is then attributed to the incorporation of NH_3 which was seen to provide a sufficient source of active nitrogen species to relieve the low catalytic activity of sapphire and a low adsorption coefficient of nitrogen. This novel approach not only simplifies the h-BN fabrication process but also brings to the fore the possibility of direct growth on microelectronic-compatible dielectric substrates, as it does away with the transfer process from metal substrates and hence the potential for contamination and mechanical damage.

In the present study, doping a few-layer h-BN with carbon (C) has further been pursued by co-introducing methane (CH_4) and NH_3 into the growth process, hence proving another broad application of the method. This C-doped h-BN material was proposed to be an improved semiconductor material and used to fabricate a deep ultraviolet (DUV) photodetector with improved performance characteristics in comparison to the intrinsic h-BN-based device.

4. Conclusion

In conclusion, this comprehensive exploration into the field of solar-blind photodetectors, particularly focusing on the advancements and challenges associated with ultrawide bandgap (UWBG) semiconductors, highlights the cutting-edge technologies shaping the future of ultraviolet detection. The study spans various materials including AlGaN-based UV detectors, diamond UV detectors, and few-layer hexagonal boron nitride (h-BN), showcasing their unique advantages, such as high responsivity, thermal stability, and the capability to operate without the influence of visible light interference. A notable innovation presented is the development of a low-temperature direct growth method for few-layer h-BN on sapphire substrates, which not only enhances the fabrication efficiency but also opens new avenues for the integration of these materials into solar-blind photodetector applications.

The challenges of doping, epitaxial growth, and substrate optimization are addressed, with solutions that push the boundaries of current technology, enabling improved performance and reliability of solar-blind photodetectors. The future of solar-blind photodetection technology looks promising, with ongoing research focusing on achieving higher energy and functional densities in cathode materials, reducing volume changes in anode materials during cycles, and exploring new semiconductor materials that offer enhanced performance characteristics.

This study not only provides a solid foundation for understanding the current state of solar-blind photodetector technology but also points towards exciting future developments. The advancements in materials science and engineering discussed herein are pivotal for the continued evolution of solar-blind photodetectors, ensuring their critical role in aerospace, military, environmental monitoring, and beyond. As the field progresses, it remains crucial to address the existing challenges through innovative research and development efforts, paving the way for the next generation of solar-blind photodetectors that offer superior performance, durability, and application flexibility.

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