Nanoarchitectonics of Visible-Blind Ultraviolet Photodetector Materials: Critical Features and Nano-Microfabrication

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Accurate measurement of ultraviolet radiation is key to many technologies including wearable devices for skin cancer prevention, optical communication systems, and missile launch detection. Nanostructuring of wide bandgap semiconductors, such as GaN, ZnO, and SiC, promises some benefits over established commercial solutions relying on n–p type Si-homojunction technology. In the past decade, a variety of carefully nanostructured architectures have been demonstrated as efficient designs for visible-blind UV photodetectors featuring superior detectivity, thermal stability, robust radiation hardness, and very low operation bias and power consumption. Here, a comprehensive review of the latest achievements on ultraviolet photodetector materials is presented, with focus on the multiscale engineering of composition and nano-microscale morphology. The review concludes with a critical assessment and comparison of state-of-the-art devices aiming to provide guidelines and research directions for the next generation of UV photodetector materials.

1. Introduction

Ultraviolet (UV) photodetectors have drawn extensive attention in recent years owing to their broad applications including flame monitoring, missile-plume detection, and space communication. All these applications require very sensitive devices with high signal-to-noise ratio and high response speed. The ideal UV photodetector should display a high responsivity, detectivity, and quantum efficiency and a good linearity of the photocurrent as a function of the incident optical power, a low noise level, high selectivity to UV light, and a fast response kinetic. The latter is particularly important for applications where a real-time signal processing is necessary, such as in optical communication systems. While being the most common material for UV photodetectors and outperforming in most materials in term of response kinetics, silicon exhibits some intrinsic limitations including an extremely poor selectivity against visible and infrared photons, and degradation under UV irradiation.

Wide bandgap semiconductors are an important class of materials for electronic and optoelectronic devices with lasers and light-emitting diodes (LEDs) exemplary recent applications. Distinct advantages of wide bandgap semiconductors include superior radiation hardness, temperature and chemical stability, and transparency to visible light. These unique features make wide bandgap semiconductors a powerful alternative material to silicon for UV photodetectors. Many wide-bandgap materials ($E_g > 3.3 $ eV) have been investigated as building blocks for visible-blind UV photodetectors, including gallium nitride (GaN), tin oxide (SnO$_2$), titanium dioxide (TiO$_2$), silicon carbide (SiC), and zinc oxide (ZnO) (Table 1). Visible-blind photodetectors based on GaN, ZnO, and SiC have raised particular interest for use in space communications, flame and missile launch detectors, and chemical sensors. However, despite these strengths, wide bandgap semiconductors often provide inferior charge carrier diffusion lengths, internal quantum efficiency, and electron/hole recombination kinetics than silicon resulting in a poor micro-macroscale performance.

In particular, visible-blind UV photodetector-based nanostructuring of wide bandgap semiconductors is being demonstrated as an efficient strategy to overcome their intrinsic limitations and design superior UV-photosensitive materials. Recently, low-dimensional materials with wide bandgap ($E_g$) in the range of $3–6 $ eV have been proposed as building blocks for UV photodetectors. Some recent materials such as AlN and graphene/AlN attracted intense attention due to their higher responsivity ($0.067 $ A W$^{-1}$ at zero bias) and faster response (80 ns at zero bias) than that of traditional photodetectors based on thin-film and bulk structures. Very recently, Zheng et al. demonstrated a complex heterojunction device where p-type graphene covers high crystallinity AlN film. These devices had high external quantum efficiency (EQE) of up to 42.6% and a response time of 80 ns at zero bias, which is $10^6–10^7$ times faster than that of currently reported photoconductive-type vacuum UV (VUV) devices. This high performance is attributed to the high mobility and high hole collection efficiency of the graphene window.
Low-dimensional materials are usually classified into 0D,[19,20] 1D,[21,22] and 2D,[23] Quantum dots (QDs),[23] nanotubes,[24] nanowires,[25] nanorods,[18,26] nanobelts,[22a,27] core/shell structures,[28] nanostructure arrays,[19a,29] epitaxial film, and heterostructures[30] are regarded as the future building blocks of visible-blind UV photodetectors. Compared to traditional thin-film and bulk materials, low-dimensional nanostructured UV photodetectors are usually characterized by higher reponsivity and photocurrent gain,[1c,31] due to their high surface-area-to-volume ratios and the nanoscale confined carrier transport kinetics.[3c,9,25b,32] The large surface-to-volume ratio significantly increases the number of surface trap states that can prolong the photocarrier lifetime by delaying the electron-hole recombination process.[1b,3c,9] In fact, the photoexcited carriers can be trapped by surface trap states and in that case their decay dynamics is dominated by the escape time from the traps.[33] The reduced dimensionality can confine the charge carrier transport path shortening the transit time and reducing recombination events.[3c]

Nanostructured wide bandgap UV photodetectors have been produced by several methods, such as magnetron sputtering,[34] pulsed laser deposition,[35] chemical vapor deposition[36] flame spray pyrolysis,[2d,9,15] and sol–gel.[17] A critical aspect remains how to accurately control the composition and hierarchical arrangement from the atomic scale of surface and bulk defects to the microscale of the active device area. The latter has been shown to be a dominant feature resulting in significant variation in the UV light response of quasi-identical nanomaterials.[9,25b,38] For instance, ZnO nanowires are usually reported to achieve orders of magnitude higher responsivity and detectivity than nanothin ZnO films. Similarly, ultraporous nanoparticle networks have shown thousand folds higher photo to dark-current ratios than more densely arranged ZnO nanoparticle layers resulting in among the highest detectivity reported for such 0D materials.[3c,9,39]

Here, we present a comprehensive review of the latest achievements and research directions on the multiscale engineering of wide bandgap semiconductor materials for photodetection of UV light. We will focus on the impact of the nano- to microscale material hierarchy discussing commonalities and discrepancies across materials and morphologies. We will conclude with a review of the rapidly emerging trends and promising strategies for overcoming remaining issues for the engineering of the next generation of miniaturized wide bandgap semiconductors UV photodetectors for wearable and easily deployable devices.

2. Photodetection Mechanism

Wide bandgap semiconductors have been investigated in many recent studies to understand the fundamental processes and enhancing the response to the UV light.[9,15,25b,40] The photoresponse characteristics of nanostructured devices are significantly influenced by a number of factors, such as the concentration of defects,[3c,9c] crystallographic orientation,[41] bandgap,[15,42] grain size,[15,34] and processing condition.[43] These factors significantly influence the photoresponse behaviors explaining the large variation in performance previously reported by various groups for similar materials.[3c,9,39]
| Material | Nanostructure | Dimension | Responsivity [A W⁻¹] | Bias [V] | $I_{dark}$ [µA] | $I_{UV}$ [µA] | $I_{UV}/I_{dark}$ | Intensity [mW cm⁻²] | $T_I$ [s] | $T_R$ [s] | Refs. |
|----------|---------------|-----------|----------------------|---------|----------------|----------------|------------------|-----------------|----------|----------|-------|
| ZnO      | NWs           | $D = 120$ nm, $L = 3$ µm | 0.07 | 20 | 0.15 | 1.8 | 12 | 0.025 | – | – | [137] |
| ZnO      | NWs           | $D = 30$–50 nm, $L = 5$ µm | 0.005 | 2 | 2 | 15 | 7.5 | 1 | 45 | 55 | [133b] |
| ZnO      | NWs           | $L = 1.2$ µm | 0.46 | 2 | 0.0486 | 0.1274 | 2.6×10⁻¹ | – | – | 4 | [133c] |
| ZnO      | NWs           | $L = 40$ µm | 0.5 | 5 | 100 | 400 | 4 | 14 | =10 | =10 | [36b] |
| NPs      | NWs           | $D = 30$ nm | – | 5 | $15 \times 10^{-6}$ | $7.9 \times 10^{-3}$ | $4.6 \times 10^{1}$ | 0.45 | 32.2 | 7.8 | [64] |
| NPs      | NWs           | $D = 150$–300 nm, $L = 10$–15 µm | – | 5 | 0.01 | 100 | $10^{4}$ | 40 | – | – | [25b] |
| NPs      | NWs           | $D = 150$ nm, $L = 10$ µm | – | 1 | $0.13 \times 10^{-5}$ | – | $10^{1}$ | 1.3 | 40 | 300 | [60a] |
| NPs      | NWs on graphene | – | 13.8 | 8.5 | 130 | 630 | =5 | 18 | 0.3 | 6.5 | [63b] |
| NPs      | NRs           | $D = 60$–70 nm, $L = 1.5$ µm | – | 5 | – | 13 | 85 | – | >500 | 500 | [138] |
| Microtubes | NWs      | $D = 100$ nm | – | 5 | 1.5 | 900 | 600 | 21.7 | 5.9 | 638 | [139] |
| Microtubes | NPs      | $D = 19$ nm | 13 | 5 | 3.61×10⁻¹ | 1200 | 3.4×10⁵ | 0.1 | 250 | 150 | [9] |
| Microtubes | NPs      | $D = 18$ nm | 6.8 | 1 | $22 \times 10^{-6}$ | 205 | $9.3 \times 10^{6}$ | 0.086 | – | – | [15] |
| Microtubes | NPs      | $D = 16$ nm | 7 | 1 | $22 \times 10^{-6}$ | 205 | $9.3 \times 10^{6}$ | 0.086 | 145 | 181 | [2d] |
| Microtubes | NPs      | $D = 18$ nm | 12 | 1 | $18 \times 10^{-6}$ | 344 | $1.9 \times 10^{7}$ | 0.080 | 5 | 9 | [3c] |
| Microtubes | NPs      | $D = 17$ nm | 0.014 | 0.2 | $1.32 \times 10^{-4}$ | 0.44 | $3.3 \times 10^{4}$ | 0.086 | 250 | 150 | [1b] |
| Microtubes | NPs      | $D = 10$ nm | – | 5 | $7 \times 10^{-6}$ | 1.8 | $2.6 \times 10^{1}$ | 0.83 | – | – | [39] |
| Nanoneedles | NWs       | $D = 50$–200 nm, $L = 50$–200 µm | – | 0.3 | – | 0.25 | 312 | 15 | 22 | 7–12 | [44] |
| Nanoneedles | NPs      | $D = 19$ nm | 13 | 5 | 3.61×10⁻¹ | 1200 | 3.4×10⁵ | 0.1 | 250 | 150 | [9] |
| Nanoneedles | NPs      | $D = 18$ nm | 6.8 | 1 | $22 \times 10^{-6}$ | 205 | $9.3 \times 10^{6}$ | 0.086 | – | – | [15] |
| Nanoneedles | NPs      | $D = 16$ nm | 7 | 1 | $22 \times 10^{-6}$ | 205 | $9.3 \times 10^{6}$ | 0.086 | 145 | 181 | [2d] |
| Nanoneedles | NPs      | $D = 18$ nm | 12 | 1 | $18 \times 10^{-6}$ | 344 | $1.9 \times 10^{7}$ | 0.080 | 5 | 9 | [3c] |
| Nanoneedles | NPs      | $D = 17$ nm | 0.014 | 0.2 | $1.32 \times 10^{-4}$ | 0.44 | $3.3 \times 10^{4}$ | 0.086 | 250 | 150 | [1b] |
| Nanoneedles | NPs      | $D = 10$ nm | – | 5 | $7 \times 10^{-6}$ | 1.8 | $2.6 \times 10^{1}$ | 0.83 | – | – | [39] |
| TiO₂      | NWs           | $D = 50$ nm, $L = 300$ nm | 6.85×10⁻⁶ | 5 | $0.03 \times 10^{-3}$ | $1.62 \times 10^{-3}$ | 54 | 0.54 | – | – | [133a] |
| TiO₂      | NPs           | – | 0.003 | –1 | $2 \times 10^{-6}$ mA cm⁻² | $=0.01$ mA cm⁻² | =50 | 3.2 | – | – | [121] |
| TiO₂      | NPs           | $D = 100$ nm, $L = 1–2$ µm | 0.01 | –1 | –0.054 | –3.5 | 65 | 1.25 | 1.4 | 6.1 | [13] |
| TiO₂      | NPs           | $D = 100$–150 nm | 0.025 | 0.6 | $=0.02$ | 5 | – | 1.25 | 0.15 | 0.05 | [133b] |
| TiO₂      | NPs           | $D = 80$ nm, $T_I = 7$ µm | 13 | 2.5 | 0.01 | 250 | $2.5 \times 10^{4}$ | 1.06 | 0.5 | 0.7 | [4] |
| TiO₂      | Epitaxial film | $T_I = 200$ nm | 3.63 | 10 | $1.4 \times 10^{-3}$ | 48 | $3.4 \times 10^{1}$ | 1.8 | – | – | [30b] |
| GaN      | NWs           | $D = 100$ ± 50 nm, $L = 1$ ± 0.2 µm | 25 | 1 | 43 | 128 | 3 | 0.2 | – | – | [133f] |
| GaN      | NWs           | $D = 50$ ± 20 nm, $L = 0.9$ ± 0.1 µm | 0.47 | –1 | 0.04 | 0.8 | 200 | 1.8 | – | – | [75c] |
| GaN      | NWs           | $T_I = 15$–20 µm | 70.4 | 5 | 0.056 | 51 | $9 \times 10^{2}$ | – | – | – | [106c] |
| GaN      | GaN-based p–i–n | – | 0.23 | 5 | $0.02 \times 10^{-3}$ | – | $6.7 \times 10^{1}$ (UV/Vis) | – | – | – | [134e] |
| GaN      | Film/Ag NPs   | $T_I = 0.3$ µm | 4 | 5 | $0.5 \times 10^{-3}$ | – | – | – | – | – | [11b] |
| GaN      | InGaN film   | $T_I = 1.5$ µm | 3.3 | –3 | $13 \times 10^{-3}$ | 4.5 | 353 | 0.97 | – | – | [134f] |
| GaN      | InGaN/GaN    | $T_I = 3.5$ µm | 0.36 | 5 | $0.022 \times 10^{-3}$ | – | $2 \times 10^{3}$ (UV/Vis) | – | – | – | [134d] |
| AlGaN    | (MSM)        | $T_I = 1$ µm | 0.14 | 10 | $=10^{-9}$ | $=10^{-2}$ | >$10^{6}$ | 0.0874 | – | – | [140] |
The most common UV photoresistor is ZnO, which has been investigated in detail by a number of groups resulting in excellent photodetection performance.\cite{14,2b,9,44} The high performance of ZnO is attributed to oxygen-related hole-trap states at the photodetector surface.\cite{2b,45} In fact, the surface traps tend to adsorb oxygen molecules from the air causing capture of free electrons from the n-type semiconductor (Figure 1a,c).\cite{9,25b} This leads to the formation of an electron depleted region near the surface and band bending, which significantly decreases the device's conductance (Figure 1a,c).\cite{9,25b} The surface band bending establishes an internal electric field, which spatially separates photogenerated electron–holes leading to suppressed photocarrier recombination and dramatically prolonging carrier life-times.\cite{2d,3c,21,14b} These effects are particularly prominent in nanocrystalline films, where the surface area is large and the depletion regions may extend throughout the entire film.\cite{1b,3d,9a}

Upon illumination with photon energy higher or equal to the semiconductor bandgap, electron–hole pair are generated.\cite{46} In the case of an n-type semiconductor, the electrons in the valence band (VB) are excited to the conduction band (CB) with simultaneous generation of the same number of holes in the VB (Figure 1b,d).\cite{25b} The holes that migrate to the surface along the potential gradient produced by band bending either discharge the negatively charged adsorbed oxygen ions to photodesorb oxygen from the surfaces or effectively get trapped at the n-type semiconductor surfaces (Figure 1b,d).\cite{9,25b} This results in an increase in the free carrier concentration and a decrease in the width of the depletion layer (Figure 1b,d). When the UV illumination is switched off, the residual accumulated holes recombine with the unpaired electrons, while oxygen is gradually reabsorbed into the surface resulting in a slow current decay.\cite{9,25b}

However, the transduction of photoresponse on the semiconductor conductivity, and thus photocurrent, depends mainly from the ratio between the Debye length ($\delta$) and the primary particle size ($d_p$). If $d_p$ is larger than twice $\delta$ then a light-insensitive conduction channel is formed (Figure 1e). This leads to relatively high dark current and exposure to UV light results only in the modulation of the conduction channel width. Decreasing this channel and thus the particle size increases the contribution of the light-sensitive domains to the total film conductivity resulting in higher photoresponse. Usually, a main distinction is made for $d_p >> 2\delta$ where the sensing mechanism is controlled by electron transport at the grain boundary and $d_p > 2\delta$ where a significant portion of the bulk participate to light sensing (Figure 1e). In contrast, if $d_p \leq 2\delta$ then the whole particle is electron depleted (Figure 1e). This leads to highly resistive films with very low dark currents. For this ultrafine structures, exposure to ultraviolet light create a conduction...
channel resulting in a drastic increase in electrical conductivity and, potentially, very high photocurrents.

3. Nanostructured Photodetector Architectures

3.1. 0D Nanostructures

QDs are small semiconducting nanocrystals (2–10 nm)\(^4^7\) that can be made of a variety of different elements, such as silicon (Si),\(^4^8\) cadmium selenide (CdSe),\(^4^9\) or cadmium sulfide (CdS).\(^2^3^b,5^0\) The size, energy levels, and emission color of QDs can be precisely controlled, which makes them extremely useful in a variety of applications.\(^2^3^a,4^7\) Because of their reduced size, QDs behave differently from bulk solids due to the quantum-confinement effects that impart unique properties.\(^4^7\) The spectral absorption of QDs is strongly related to their size (Figure 2a) as their bandgap is affected by quantum confinement.\(^2^3^a\) The light excitation of QD by UV light usually results in the emission of lower energy photons in the visible spectrum. For most quantum dots, their size affects the allowed quantum states for electrons and holes, the charge-carrying particles in the material. These states determine the energies and therefore the colors of the emitted photons.\(^5^1^4\)

History of QDs begins with their first discovery in glass crystals in the 1980s by Ekimov and co-workers at the IOFFE Physical-Technical Institute in St. Petersburg.\(^5^2\) They noticed unusual optical spectra from samples of glass containing the semiconductors cadmium sulfide or cadmium selenide.\(^5^2\) Systematic advancement in the science and technology of QDs came after 1984, when Brus discovered the relation between size and bandgap for semiconductor nanoparticles.\(^5^3\) However, it took nearly a decade for a new level in QD research to reach with the successful synthesis of colloidal Cd\(_x\)(X = S, Se, Te) QDs with size-tunable bandedge absorption and emissions.\(^5^4\) To date, various methods have been developed to synthesize monodisperse and solution-stable QDs of less than 10 nm, including hydrothermal method,\(^5^5\) electrochemical strategies,\(^5^6\) the solution chemistry method,\(^5^7\) and the ultrasonic and microwave method.\(^5^8\)

3.2. 1D Nanostructures

3.2.1. Nanowires

Nanowires are 1D nanomaterials with diameters in the order of a few hundred nanometers or less, and lengths ranging from several hundreds of nanometer to few centimeters.\(^5^9\) Because of their nanoscale dimensions in the radial direction, they have size confinement effects that give them novel physical properties compared to bulk materials. Benefiting from a large surface-to-volume ratio and a Debye length comparable to their small size, 1D semiconductor nanostructures are considered among the most promising building blocks for photodetectors with high sensitivity, quantum efficiency, and fast response speed.\(^6^0\) The length and diameter of nanowires as well as their alignment

![Figure 2.](image-url) a) Colloidal quantum dots irradiated with UV light. Different sized quantum dots emit different color light due to quantum confinement. SEM image of b) regularly patterned ZnO nanorods grown with the hydrothermal method,\(^6^2\) c) belt-like structure fabricated by an improved vapor–liquid–solid (VLS) process with a uniform belt thickness of \(\approx\)200 nm,\(^6^2\) and d) ZnO nanodisk with a diameter of 5 \(\mu\)m fabricated by drop-casting process.\(^6^2\) Cross-sectional SEM image of e) dense TiO\(_2\) structure grown on silicon slot structures using atomic layer deposition technique,\(^6^3\) f) porous TiO\(_2\) film on the silicon substrate fabricated by spin-coating technique,\(^6^4\) and g) ultraporous nanoparticles network made by flame spray pyrolysis.\(^6^5\) (a,b) Reproduced under the terms of an open-access unported license (CC-BY 3.0).\(^1^2^9\) Copyright 2014, The Authors. (c) Reproduced with permission.\(^2^2^a\) Copyright 2010, Wiley-VCH. (d) Reproduced with permission.\(^2^2^b\) Copyright 2014, American Chemical Society. (e) Reproduced with permission.\(^7^5^4\) Copyright 2010, OSA Publishing. (f) Reproduced with permission.\(^1^1^0\) Copyright 2012, Royal Society of Chemistry. (g) Reproduced with permission.\(^6^6\) Copyright 2015, Wiley-VCH.
affect the light absorption properties and need to be controlled since they dominate the physical, chemical and optical states of the nanowire.\cite{12a,59a,61} In fact, the critical device size is defined during the growth process and can be controlled with atomic scale resolution. A key issue related to the growth of nanowires is how to induce 1D crystal growth in a controlled manner. Regarding this, many approaches have been studied, including vapor–liquid–solid (VLS),\cite{62} chemical vapor deposition (CVD),\cite{36b,63} wet synthesis,\cite{64} and pulsed laser deposition (PLD).\cite{22b}

3.2.2. Nanorods

Nanowires and nanorods are similar 1D structure with the main distinction being their length to diameter ratios. Nanowires are 1D nanostructures, which generally have diameters of the order of tens of nanometers, with unconfined length scales. They have length to diameter ratios of up to 1000, while nanorods have aspect ratios below 10. Similar to nanowires, nanorods with diameters between 1 to 500 nm (Figure 2b), have been focus of considerable attention due to their potential to answer fundamental questions on 1D systems and their critical role in different applications ranging from molecular electronics to novel scanning microscopy probes.\cite{32,65} For nanorod-based devices, it is important not only to grow nanorods with a high degree of regularity and uniformity in terms of their height and cross-sectional size, but also to accurately control their positions.\cite{18,66} (Figure 2b).

3.3. 2D Nanostructures

Nanobelts, presenting an intermediate structured between one and 2D materials (Figure 2c), have been intensively studied in the last few years, due to their advantage as a quasi-ideal system to study dimensionally confined transport phenomena and building functional devices along individual nanobelts.\cite{2a,22a,67} They were first reported by Wang and co-workers\cite{68} in 2001 as a structurally controlled nanomaterial with well-defined facets, unique growth directions, and a typical rectangular cross section. With large surface areas exposed to the light, various kinds of nanobelts have been assembled into nanoscale optical devices.\cite{121,122}

As mentioned previously, nanostructured materials with lower dimensionality can lead to higher optical responses as compared to their bulk counterparts. In fact, the electron and hole energy states become discrete due to the spatial confinement, which can prolong the photocarrier lifetime.\cite{69} However, the electrical performance of QD devices is limited due to the severe scattering from a very large number of grain boundaries within the QD device with the nanoscale grain size.\cite{70} For the 1D materials, the incomplete surface coverage is considered as a drawback for their photodetection performance.\cite{71} Therefore, ultrathin 2D nanostructures are more able to satisfy the requirements of ultrathin structures, low-cost, portability, and mechanical stability in high performance flexible optoelectronic devices.\cite{72} In addition, it has been reported that polar facets of some nanostructures, such as ZnO, contain more oxygen vacancies than the other facets, which have a significant impact on the electronic properties and enhance the efficiency of the electron–hole separation.\cite{22b,73} Hence, the efficient separation of charges and the low dimensionality of the conductive volume should be particularly significant for the presented thin nanodisks (Figure 2d) combining large surface-to-volume ratio and polar exposed facets.\cite{22b} In fact, the high quality of single crystal ZnO nanodisks and nanosheets results in a reduction of the disadvantageous effects of grain boundary recombination, as well as enhancing carrier transport, providing a high active area of the charge carriers. Compared to the QDs 0D structure and the nanowires, nanorods and nanoribbons 1D structure, the 2D structures can be more compatible with available microfabrication techniques, and can be more easily transformed into more complex structures.\cite{74}

3.4. Nanostructured Films

3.4.1. Dense Films

Nanostructured dense films (Figure 2e) fabricated by different methods such as atomic laser deposition (ALD) and molecular beam epitaxy (MBE) have been investigated in the past decades as UV photodetectors resulting in fast photoresponse to UV illumination.\cite{75} Ultrathin nanostructured films are of particular interest due to quantum confinement effects. The optoelectronic properties of nanometer-thick films, however, are often controlled by surface-dominated phenomena.\cite{98,130} As a result, extremely thin films with thickness comparable to the Debye length of the semiconductor are required to ensure the participation of the whole structure in the photodetection mechanism avoiding the formation of non-electron-depleted domains.\cite{13c,9} However, this ultralow thickness might result in low conductivity, poor mechanical stability of the device and very low optical densities.\cite{76}

3.4.2. Porous Films

Porous nanostructured films (Figure 2f) are the most common morphologies for UV photodetectors due to their high specific surface area and optical density.\cite{9,77} Several methods, such as hydrothermal,\cite{78} sol–gel, and numerous wet synthesis methods\cite{79} have been utilized previously to fabricate porous nanostructure films as UV photodetectors. Compared to the dense films, porous structures can enhance light harvesting by reducing the reflection and the transmission.\cite{130} Two mechanisms are responsible for highlight absorption in porous films. One is the large film thickness and the other is the stronger light scattering in a porous sample.\cite{80}

3.4.3. Ultraporous Films

Very recently, ultraporous nanoparticle networks with up to 98% porosity have been reported\cite{15,2d,9,9,15} as a highly performing superstructural design (Figure 2g) for visible-blind UV photodetectors. In addition to the particle morphology,\cite{35c} film thickness\cite{81} and grain necking,\cite{73} a key structural
property impacting the performance of wide bandgap photodetectors is the film porosity.\cite{1h,2d,3c,9,15} Figure 3a,b present the I–V characteristic of spin-coated porous nanostructure (Figure 3a) and flame-made ultraporous ZnO nanoparticle-based photodetectors\cite{9} (Figure 3b) at a bias of 5 V and UV light density (LD) of 830 and 100 μW cm−2, respectively. This comparison revealed a ~60 times lower photocurrent density of 0.57 μA mm−2 for spin coated porous structure even under eight times higher LD (830 μW cm−2) (Figure 3a).\cite{10} While the ultraporous structure resulted in photocurrents density of above 34.28 μA mm−2 at low light density of 100 μW cm−2 (Figure 3b).\cite{10} As a result, it is has been suggested that ultraporous structures may have a superior performance as photodetectors. They offer several advantages such as high photocurrents (milliamperes), low dark currents (nanoamperes) and detection limit of low light densities at low operation voltages.\cite{1h,2d,3c,9,15} In fact, the strong penetration of light in these ultraporous nanostructures allows photoexcitation of the bottom layers of the device resulting in significantly higher light absorption and electrical conductivity compared to the other nanostructured films.\cite{9,19} In contrast, for the porous structures with the film porosity between 40% and 60%, the higher proportion of UV light might be absorbed by the top layers of the device, which are not sufficiently close to the electrodes,\cite{19} resulting in absorption of significantly smaller fraction of incoming UV light in bottom layers of the film.

4. Materials

Several wide bandgap semiconductors have been explored as promising materials for various photodetection applications, such as chemical, environmental, and biological analysis, monitoring flame and radiation detection, astronomical studies, and optical communications. In this section, recent progresses in UV photodetection properties of several wide bandgap semiconductors, including TiO2\cite{4,30a,82}, SiC\cite{14b,83}, ZnO\cite{1d,9,39,60b}, GaN\cite{84} and SnO2\cite{12a,85} area discussed.

4.1. SiC-Based Photodetectors

SiC is considered as one of the most important wide bandgap materials (~2.2–3.0 eV)\cite{86} in the development of UV photodetectors because of their large gains, high signal-to-noise ratios, and visible light-blind response.\cite{14b,87} These properties make SiC a promising material for monitoring the UV spectrum without the need of visible-light filters.\cite{88} Furthermore, semiconductor SiC offers a high thermal conductivity (~120 W m−1 K−1),\cite{89} high hardness and Young's modulus (typically ~450 GPa compared with ~130 GPa for Si),\cite{90} and an outstanding long-term stability even under high-intensity UV radiation and high operating temperature.\cite{14b,88b} This combination of excellent electronic and mechanical properties offers many possibilities for using SiC as a material for a wide range of sensors, particularly in applications featuring high temperatures or hostile environments.\cite{81,91} However, the current response time of these devices is very slow (e.g., > 15 s), which limits their applicability in real time signal processing applications including optical communication systems and military applications.\cite{14b}

The SiC exists in a large number of polytypes, which are different crystal structures built from the same Si–C subunit organized into a variety of stacking sequences.\cite{92} There are over 100 of these polytypes known,\cite{93} but the majority of research and development has focused on 3C, 6H, and 4H\cite{86a,87,94} polytypes. Among them, the 4H–SiC (3.2 eV)\cite{95} is the most common polytype for electronic devices due to its overall superior material properties.\cite{96} Typically, 4H–SiC-based UV photodetectors have a photo-response from 200 to 380 nm wavelengths and a peak responsivity at around 290 nm.\cite{96}

Nanostructured SiC has superior properties compared to bulk SiC for applications in light-emitting diodes and UV photodetectors. The first commercial nanostructured photodetector device based on SiC was fabricated with p-type 6H–SiC in 1993\cite{97} and
presented a low dark current of about 100 nA cm$^{-2}$ at 1.0 V at a temperature of 200 °C. Recently an increasing number of research groups have paid attention to the development of high-performance UV photodetectors using 4H–SiC material systems.[14b,96b,c,98] For example, by using laser plasma deposition system, Aldalbahi et al.[14b] developed a 2 µm thick SiC film on Si-wafer with a responsivity of up to 0.18 A W$^{-1}$ at illumination density of 2 mW cm$^{-2}$, which is significantly higher than that of SiC UV detectors previously reported (0.03–0.08 A W$^{-1}$).[98a,99] In addition, a response time of 18 s under 350 nm wavelength of incident radiation was observed.[14b]

4.2. GaN-Based Photodetectors

GaN with a room-temperature bandgap of 3.39 eV (366 nm) is among the most promising material for semiconductor photonic devices operating in the UV regions of the spectrum.[59a,60b,84c,100] The high transparency of high quality GaN at wavelengths longer than its bandgap makes it an ideal material for photodetectors capable of not-responding near infrared and visible regions of the solar spectrum while retaining near unity quantum efficiency in the UV.[11b] The superior radiation hardness and high temperature resistance of GaN makes the fabricated devices suitable for working in extreme conditions.[102] Moreover, by using its alloys with aluminum and indium, the cut-off wavelength are tunable in the range from 366 to 200 nm.[103]

Various types of GaN-based photodetectors have been reported, including p–n junctions,[3b,75c,104] Schottky barrier photodetectors,[105] solar-blind ultraviolet photodetectors,[106] and UV avalanche photodiodes.[107] The motivation to investigate p–n photodetectors is to take advantage of its structure for better sensitivity and faster response.[3b,75c,104] Sun et al. reported a unique structure for self-driven GaN-based photodetectors, by adopting interdigitated Schottky and near-ohmic contacts. They deposited the GaN epilayer on a sapphire substrate using metal-organic chemical vapor deposition (MOCVD) and then, added three typical interdigitated finger structures of Ni/GaN/Ag, Ni/GaN/Cr, and Ni/GaN/Ti/Al on the top of GaN layer (Figure 4a). The different interdigitated Schottky and near-ohmic contacts resulted in a fall in the Schottky barrier, and thus in band bending. The band diagrams of the detectors before and after illumination are illustrated in Figure 4b. The greater the difference between interdigitated Schottky barriers, the greater the band bending, resulting in a high responsivity of 0.104 A W$^{-1}$ at 0 V bias for Ni/GaN/Ti/Al detector (Figure 4d). Other Schottky structure has also been explored for GaN Schottky barrier photodetectors since it does not need the realization of p-type GaN material. However, fabricating high performance GaN Schottky barrier ultraviolet photodetector is still challenging due to the problem of surface states, which increase the recombination of photogenerated electron–hole pairs.[11a,108] To accelerate the development of GaN Schottky barrier photodetectors, it is necessary to reduce the negative influence of surface states on their performance.

In another approach, Jia et al.[109] developed a dual-band plasmonic GaN photodetector with high sensitivity to both UV and green light. They fabricated Ga-polar GaN films (with 4 µm thickness) on sapphire substrates (Figure 4c) using the hydride
vapor phase epitaxy method. Later, irregular hemispherical Au nanoparticles were deposited on GaN film (Figure 4c, inset), using sputtering technique. This Au nanoparticles decoration resulted in a significant increase in the device responsivity in comparison to the blank GaN photodetector. The enhancement ratios for UV and green lights were ≈54 and ≈64 times, respectively (Figure 4e). This higher photodetecting property is attributed to polarization enhanced charge transfer of excited hot electrons from Au nanoparticles to GaN film (Figure 4f).[109]

In a similar research,[11b] nanoplasmonic enhancement using Ag nanoparticles was proposed as a great method for improving the performance of GaN-based devices. Li et al.[11b] have reported that through the excitation of the surface plasmon, the incident light interacts with Ag nanoparticle and significantly enhances the scattering cross section (Figure 5a–c). They have grown a ≈3 µm thick GaN epilayer on a sapphire substrate using MOCVD and Ag metal nanoparticles were deposited on the surface of GaN by electron beam evaporation (Figure 5a). The responsivity of the fabricated device increased by a factor of 30 with annealed Ag nanoparticles on the GaN surface from 0.148 to 4.0 A W⁻¹ (Figure 5d).[11b]

4.3. SnO₂-Based Photodetectors

Among a variety of semiconductor compounds available for UV detecting application, SnO₂ is a very interesting n-type semiconductor with a wide direct bandgap of ≈3.6 eV (~340 nm)[12b,35a] and transparency to visible light,⁹⁹b,110 and thus has been proposed to be applied as a potential material for visible-blind photodetectors.[30a,77b] In addition, SnO₂ found its application in field emission since it has a relatively low work function (4.7 eV)[111] in contrast to carbon nanotube (5 eV)[112] and ZnO (5.3 eV).[113] The electrical conductivity of intrinsic SnO₂ depends strongly on the surface properties of this material. In fact, surface molecular adsorption/desorption affects the band modulation and space-charge layer, which make SnO₂ an important conductance-type gas-sensing material.[114] Due to the complicated spatial arrangement, the hierarchical architectures can provide extraordinarily high activated surface area[114c,d] and also robustness.[115] Thus far, the reported SnO₂ nanostructures are mostly 1D structures, such as nanowires,[116] nanorods,[26,117] nanobelts,[67a,118] and nanowires.[24]

Recently, a thin SnO₂ nanowire photodetector with diameter of 26 nm (Figure 6a) and a length of about 30–40 µm, resulting in a projected surface area of 0.78–1.04 µm², was fabricated by a facile VLS process with Au-layer as catalyst (Figure 6b).[12a] The fabricated photodetector exhibited a photocurrent and dark current of 2.1 µA and 19.4 nA with Iₚ/Iₖ ratio of 10² (Figure 6c) under an applied bias of 1 V and 320 nm light illumination with a density of 0.91 mW cm⁻².[12a] The responsivity estimated from the project nanowire area (1 µm²) is 2.3 × 10⁵ A W⁻¹. In another approach,[12b] a 2D SnO₂ monolayer nanofilm (Figure 6c,d) was fabricated using an oil–water interfacial self-assembly method resulting in a significantly higher photocurrent of 375 µA (Figure 6f) at the same light illumination and applied bias. However, the device exhibited low photo- to dark-current ratio of only 4 due to a significantly higher dark-current of 90 µA (Figure 6f).[12b]

This higher dark current is attributed to the significantly larger number of nanoparticle neighbors in the 2D SnO₂ monolayer film that results in higher electrical conductivity.[9] In fact, this low photo- to dark-current ratio is attributed to poor penetration of light into the film limiting the photo-excitation to the top film layers.[9] Higher thickness of the 2D SnO₂ monolayer (94 nm)[12b] compared to a thinner diameter of the SnO₂ nanowire (less than 26 nm) fabricated by Hu et al.[12a] might
lead to formation of gas-tight SnO₂ domains, which are not electron depleted and thus less sensitive to light (Figure 6e).[89] While in the case of nanowire device, a higher volume fraction of the nanowire is electron-depleted in the dark condition resulting in considerably lower dark-current of only 19.4 nA (Figure 6f) [12a] at the applied bias of 1 V.

In another approach, Deng et al.[85] fabricated 3D SnO₂ nanowire arrays on a carbon cloth template using combined processes of atomic layer deposition and vapor transport (Figure 6g). A thin film of Au was introduced on SnO₂ nanowires as the catalyst through electron beam evaporation (Figure 6g), followed by a post-heat treatment to form the flexible nanostucture.[85] This resulted in a hollow hierarchical structure of nanowire arrays with the diameter of about 60 nm (Figure 6h). The fabricated photodetector exhibited a dark current of only 2.3 pA (Figure 6i), which is much lower than those previously reported in literature. In addition, the device photocurrent reached to 0.5 nA under 350 nm light illumination by applying a low voltage of 1.0 V (Figure 6i). A larger photocurrent could be achieved at a higher applied bias. This high photodetecting performance was attributed to the extremely high density, quasi-aligned arrangement and a large aspect-ratio of SnO₂ nanowires.[85]

4.4. TiO₂-Based Photodetectors

TiO₂ is a well-known transparent conductive oxide (TCO), which is particularly suitable for UV detection against a background with infrared and visible light.[4,13] Due to the appropriate bandgap (3.2 eV for anatase[82b,119] and 3.0 eV for rutile[120]), distinctive absorption characteristics,[121] high refractive index,[82a,122] and low fabrication cost, TiO₂ is emerging as a promising material for photodetectors. With large specific surface areas, 1D TiO₂ nanostructures gained special attention in recent years due to their excellent performance in many well-known research areas.[4,65b,120b]

Recently, 1D nanostructure of assembled freestanding TiO₂ nanorod cloths (TNRCs) from a fast and catalyst-free microwave heating route with post heating treatment at 800 °C (Figure 7a,c). This novel hierarchical structure of interlaced hollow fibers with nanorods on the surface can be readily transferred onto a fluorine-doped tin oxide (FTO), Ti foil and polyethylene terephthalate (PET) providing a promising way to develop devices for applications in many emerging research fields, such as flexible solar cells[123] and flexible electronic devices (Figure 7c, inset).[61]

Their fabricated TNRC-based photodetectors illustrated a good sensitivity (Iₚ/Iₗ) of ≈7, which was defined as the ratio of the photocurrent under illumination at different wavelengths of 365 and 254 nm.[13] However, the device exhibited a low responsivity (0.015 A W⁻¹) under light illumination of 1.25 mW cm⁻² and the applied bias of −1 V. In another approach, Zou et al.[4] reported a very high UV-sensitive photoconductance of pure TiO₂ nanotube arrays (Figure 7b,d) made by electrochemical anodization, which resulted in a fast response with rise time and decay time of only 0.5 and 0.7 s, respectively.[4] The high responsivity of 13 A W⁻¹ was also found under 1.06 mW cm⁻² UV (312 nm) illumination at 2.5 V bias (Figure 7d).[10] This high responsivity mainly comes from the internal gain induced by desorption of oxygen from the nanotube large surfaces (Figure 7b,d, inset) and the reduction of the Schottky barrier at TiO₂/Ag contact under UV illumination.[4,124]
In another approach, a self-powered wearable UV photodetector was developed by integrating two flexible electrodes in a matched electrolyte. As schematically illustrated in Figure 7e, a Prussian Blue (PB) electrode was deposited on a transparent flexible PET/ITO substrate using a cyclic voltammetry scan method and then, TiO$_2$ nanotubes were synthesized via an anodic oxidation process, as photoanode. After annealing at 450 °C for 30 min, the as-grown TiO$_2$ nanotubes photoanode and the PB counter electrodes put face-to-face (but not in contact) with K$_2$SO$_4$ aqueous solution separating each other. As shown in Figure 7g, the device illustrated a peak responsivity of 78.3 mA W$^{-1}$ at the wavelength of 360 nm, which clearly indicated its visible-blind feature. In addition to this high photoresponsivity to UV light, the device color changes once exposed to UV light (Figure 7g, inset). The high the UV light intensity, the larger the decoloration degree. Furthermore, the device demonstrated a photocurrent stability at different bending states. As shown in Figure 7f, the output photocurrent in the device remained nearly unchanged regardless of the bending states.

4.5. ZnO-Based Photodetectors

With wide direct bandgap (3.37 eV) and large exciton binding energy (~60 meV) at room temperature,[9,39,44] ZnO nanostructures are among the most investigated materials for different electronic applications, such as field effect transistors, diodes, surface acoustic wave devices, electromechanical devices, and gas sensors.[2b,9,32,64,125] Among various applications for ZnO semiconductors, the UV photodetector is an excellent device that has a wide range of chemical and environmental detecting applications.[39,63b,77b,c,126]

Figure 7. Top-view SEM images of a) the TiO$_2$/carbon cloths and b) the as-anodized TiO$_2$ nanotube arrays made by electrochemical anodization. Spectral response of c) the TNRC-based device[13] and d) TiO$_2$ nanotube array device[4] at a bias of 1 and 2.5 V, respectively. c)Inset: Optical image of the flexible carbon cloths partly grown with TiO$_2$ nanorods.[13] d)Inset: Schematic of a TiO$_2$ nanotube arrays device structure.[4] e) Fabrication procedure of the flexible UV photodetectors based on Prussian Blue/TiO$_2$ nanotube arrays.[132] f) Typical I–t curves of the flexible UV photodetector under flat and bent states at the UV intensity of 10 mW cm$^{-2}$ at the wavelength of 365 nm.[132] g) Typical photoresponsivity spectrum of the visualized and flexible UV photodetector. Inset: Digital photographs of the device placed on wrist before and after UV exposure.[132] (a,b,d) Reproduced with permission.[4] Copyright 2010, ACS Publications. (c) Reproduced with permission.[13] Copyright 2011, ACS Publications. (e,f,g) Reproduced with permission.[132] Copyright 2018, Wiley-VCH.
single-layer graphene sheets using CVD method featuring a high responsivity of \( \approx 14 \text{ A W}^{-1} \), which is significantly higher than that of ZnO-based UV photodetectors. However, considering the applied bias of 8.5 V, the device responsivity can be calculated as 1.62 A W\(^{-1}\) per volt, which is not particularly high compared to other studies. In another approach, highly performing porous films of electron-depleted ZnO nanoparticles were fabricated using spin-coating and resulted in a high responsivity of 26 A W\(^{-1}\).\(^{[39]}\) However, a very high voltage of 120 V was applied resulting in a device responsivity of 0.5 A W\(^{-1}\) per volt. In fact, simply increasing the applied voltage to increase the responsivity may not be a viable option as it may result in a significant dark-current increase. Here, assessing the responsivity per volt helps to get a more reliable comparison between studies using different voltages.

Figure 8c illustrates the device responsivity and dark current for ZnO-based photodetectors with different structural morphology, such as single nanowires, nanostructured, and nanowire films. As mentioned above, for all different nanostructured morphologies, the higher responsivity usually results from a higher dark current. Surprisingly, single nanowire devices obtained the highest UV photoresponsivity at considerably low dark currents. This high responsivity might be attributed to the effective surface area considered for the device responsivity. In fact, for single nanowire device, the cross-sectional area is usually considered as effective surface area in responsivity measurement while the entire outer area of the nanowire is exposed to UV light and may contribute to light absorption.

Recently, Liu et al.\(^{[60a]}\) have fabricated ZnO nanowires with a diameter of 150 nm (Figure 9a–c) and a length of about 10 \( \mu \)m featuring a low dark current of 9.7 pA and a photo-to-dark-current ratio of about 10\(^3\) at an applied bias of 5 V (Figure 8d) and under a light density of 1.3 mW cm\(^{-2}\).\(^{[60a]}\) In addition, they have reported that the photodetection properties of the device were improved significantly by decorating the ZnO nanowires with Au nanoparticles (Figure 9c) resulting in an ultralow dark current of 0.13 pA and \( I_{\text{photo}}/I_{\text{dark}} \) ratio of 5 \( \times \) 10\(^6\) (Figure 9d). Despite these excellent features, similar to the other ZnO-based UV photodetectors,\(^{[9,21]}\) these devices exhibited a relatively slow response speed (25 s and 40 s rise time and 10 s and 300 s decay time with and without Au decoration) due to the inherent defects, such as oxygen vacancies and zinc interstitials.\(^{[60a]}\)

In order to improve the response speed of ZnO-based UV photodetectors, Tian et al.\(^{[77c]}\) fabricated a branched architecture with ZnS backbones and ZnO branches (Figure 9f–h) to combine the fast response speed of ZnS, and excellent optoelectronic properties of ZnO. Figure 9f,g shows SEM and TEM images of the final product consisting of a large number of micrometer-sized branched architectures. Using a thermal evaporation process and a hydrothermal growth, they fabricated a flexible ZnS–ZnO heterostructure nanofilm (Figure 9e,i, inset) featuring optimized photodetecting performance, including high sensitivity (Figure 9i), fast response speed of about 0.7 s (Figure 9k) and broad UV range photoresponse (Figure 9i). In addition, the photodetecting properties of the device in vacuum condition showed an excellent improvement in photocurrent (18 time higher) compared to the ambient condition (Figure 9j), confirming the existence of oxygen chemisorption/desorption\(^{[2d,3c,9,15]}\) on the ZnS–ZnO heterostructures, and demonstrating that the device photocurrent could be enhance by decreasing the gas pressure of the environment.
In another approach, Boruah et al.\textsuperscript{[25a]} fabricated highly dense graphene/ZnO nanowire-based photodetector on glass substrates by thermal oxidation of metallic Zn thin film in air and transferring as-grown graphene onto bulk ZnO nanowires. Thereafter, reactive thermal evaporation (RTE) was used to deposit aluminum electrodes of 300 nm thickness on top of the graphene with a gap of 90 µm between the electrodes. Their devices featured significantly higher photocurrents of 1.65 mA (5 orders of magnitudes) than that of Liu et al., \textsuperscript{[60a]} at the same applied bias and light density. This higher photocurrent might be attributed to the higher optical density of ZnO nanowires compared to a single nanowire resulting in a greater number of photogenerated electron–hole pairs. However, increasing the number of nanowires resulted in a considerably higher dark current of 80 mA compared to the very low dark current of only 9.7 pA for single ZnO nanowire device. As a result, the photo- to dark-current ratio decreased from 10\textsuperscript{3} of the single nanowire to only 20 of multi-nanowires device. In fact, the device conductivity increases significantly by increasing the number of nanowires used in the photodetector. Similar results were obtained by Kind et al. \textsuperscript{[40a]} using an individual ZnO nanowire device in comparison with the results reported for low temperature synthesized vertical ZnO nanowires.\textsuperscript{[128]} In fact, under the same applied bias of 5 V and light density of 0.3 mW cm\textsuperscript{-2}, the photocurrent increased significantly from 0.25 µA of the single nanowire\textsuperscript{[40a]} to 13.5 µA of the vertical ZnO nanowires device.\textsuperscript{[128]} While the photo- to dark-current ratio decreased with more than three orders of magnitude due to a higher dark current of 0.2 µA of the multi nanowires devices\textsuperscript{[128]} compared to only 1 pA of the single nanowire ones.\textsuperscript{[40a]}

Very recently, we proposed a novel hierarchical morphology for UV photodetectors that results in excellent selectivity, low dark current (nA), and high photocurrent (mA) to low light intensities (≈80 µW cm\textsuperscript{-2}).\textsuperscript{[2d,9]} A flame spray pyrolysis (FSP) system (Figure 10a) was used for the synthesis and direct deposition of ZnO nanoparticles films onto the glass substrates (Figure 10a–d) featuring a set of interdigitated electrodes.\textsuperscript{[2d,9]} We demonstrated a rapid, one-step synthesis and self-assembly of transparent ultraporous nanostructured devices (Figure 10d–f) composed of electron-depleted crystalline ZnO nanoparticles (Figure 10f) resulting in an absorption of more than 80% of the incoming UV light and transmission of more than 90% of the visible light (Figure 10h).\textsuperscript{[2d,9]} The optimized device featured ultralow dark current of 22 pA and high photocurrent of 205 µA at a light intensity of 86 µW cm\textsuperscript{-2} and bias of 1 V (Figure 10i). The resulting \( I_{\text{UV}} / I_{\text{dark}} \) ratio (9.3 \times 10\textsuperscript{6}) was the highest so far.
reported at this light intensity (Figure 10i). However, the response dynamics of the fabricated devices was in the range of 100–200 s due to its ultrahigh porosity, and the adsorption and desorption of O$_2$ trapping states.[3b] To overcome this bottleneck, we presented a 3D coating of a 98% porous film of n-type ZnO nanoparticles with p-type NiO nanoclusters resulted in a 3D network of nanoscale heterojunctions (3DNH).[3c] The built-in electric fields between the nanoscale p- and n-type domains enable the rapid separation of the photogenerated electron–hole pairs decreasing the photocurrent rise and decay times by 26- and 20 folds, respectively (Figure 10j).[3c] The NiO nanothin coating also increases the overall photodetector properties resulting in excellent responsivities of more than 12 A W$^{-1}$, photo to dark ratios exceeding 10$^7$ and ultra-high directivities of up to 3 $\times$ 10$^{12}$ Jones at a bias of 1 V and light density of 80 $\mu$W cm$^{-2}$.[3c] In another approach, a nanoscale architecture was presented for band-selective UV photodetectors featuring excellent tunability, light detection performance, and miniaturization potential.[15] The device layout relied on the 3D integration of ultraporous functional layers of ZnO, SiO$_2$, and TiO$_2$ nanoparticles.[15] A band-selective photoresponse was obtained by exploiting the transmittance window between the indirect bandgap of TiO$_2$ and the sharp-edge of the direct bandgap of ZnO.[15] As a result, these ultraporous TiO$_2$ layers can efficiently block UVB radiation while transmitting a significant fraction of UVA (Figure 10k).[15] The bandwidth of these integrated metal-oxide nanoparticle networks (IMONNs) was tuned from 85 nm of the pure ZnO layers to 29 nm of the TiO$_2$/SiO$_2$/ZnO networks with 6.6 $\mu$m thick TiO$_2$ layer (Figure 10k).[15] This tunable architecture and nanofabrication approach are compatible with state-of-the micromachining technologies, and provided a flexible solution for the engineering of wearable band-selective photodetectors.

5. Summary and Outlook

The significant recent advances in the nanostructuring of wide bandgap semiconductors have opened the possibility of developing low-cost selective UV photodetectors, capable of operating in harsh atmospheres and featuring significantly high photodetection performances than established technologies. Significant efforts are been spent in improving the key figures of merit of these devices including responsivity, detectivity, photodetective gain, EQE%, and LDR. Different nanostructured morphologies such as 0D, 1D, 2D, and 3D nanomaterial-based devices are being carefully investigated. 1D nanomaterials with diameters of few nanometers exhibit among the best photodetection performances. In addition, a variety of wide bandgap semiconductors including TiO$_2$, SiC, ZnO, GaN, and SnO$_2$ were explored as UV photodetectors.

Overall, analysis of the trends across different materials was found that ZnO is the most investigated material for UV photodetectors applications due to its wide direct bandgap of 3.37 eV at room temperature, ease of fabrication and high transmittance for visible light. However, increasing the performance of ZnO-based photodetectors, particularly their response speed, is still one of the major issues of these types of UV photodetectors, and continuing efforts have been devoted to this issue.
In terms of nanostructured architecture, single nanowire devices illustrated the highest UV photoreponsivity at low dark current, among all other nanostructured devices, such as nanostructured and nanowires films. However, this high performance might be attributed to the effective surface area considered for the device responsivity. In addition, inducing the single nanowire growth in a controlled manner is still one of the main challenges of such nanostructure devices that still need to be addressed.

There is still plenty of room for the development of wide bandgap semiconductors and their photodetector applications. Future work should focus on novel concepts both in terms of material and device fabrications. The combination of the advantages of graphene having superior electrical conduction properties, and the distinct advantages of wide bandgap semiconductors is a promising research direction for future investigations. In addition, other nanostructured designs, such as nanoscale heterojunction UV photodetectors based on wide bandgap semiconductors and their photodetector applications. The combination of the properties, and the distinct advantages of wide bandgap semiconductors and their photodetector applications. The combination of the material and device fabrications. The combination of the advantages of graphene having superior electrical conduction properties, and the distinct advantages of wide bandgap semiconductors is a promising research direction for future investigations. In addition, other nanostructured designs, such as nanoscale heterojunction UV photodetectors based on wide bandgap semiconductors can be further accomplished to meet the demands of various applications, especially when high-speed responses are required.

Acknowledgements

This review is part of the Advanced Optical Materials Hall of Fame article series, which recognizes the excellent contributions of leading researchers to the field of optical materials science.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

GaN, nanoarchitectonics, TiO₂, UV photodetectors, visible-blind photodetectors, wearable devices, wide-bandgap semiconductors, ZnO

Received: May 2, 2018
Revised: June 26, 2018
Published online: September 6, 2018

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