



Review Research and Progress of Transparent, Flexible Tin Oxide Ultraviolet Photodetector

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Abstract: Optical detection is of great significance in various fields such as industry, military, and medical treatment, especially ultraviolet (UV) photodetectors. Moreover, as the demand for wearable devices continues to increase, the UV photodetector, which is one of the most important sensors, has put forward higher requirements for bending resistance, durability, and transparency. Tin oxide (SnO₂) has a wide band gap, high ultraviolet exciton gain, etc., and is considered to be an ideal material for preparing UV photodetectors. At present, SnO₂-based UV photodetectors have a transparency of more than 70% in the visible light region and also have excellent flexibility of 160% tensile strain. Focusing on SnO₂ nanostructures, the article mainly summarizes the progress of SnO₂ UV photodetectors in flexibility and transparency in recent years and proposes feasible optimization directions and difficulties.

Keywords: UV photodetector; SnO₂; transparent; flexible; wearable

1. Introduction

As one of the most important optoelectronic devices, UV photodetectors are hugely in demand in space communications, missile warning, ozone layer monitoring, flame detection, and spectral analysis in the medical field [1–6]. Compared with traditional UV photodetectors, which have low single detection quality in complex application environments due to rigid obstacles, flexible detectors can collect information more effectively and produce higher quality signals [7]. Particularly, transparent and flexible UV photodetectors play an important role in the progress of wearable photodetection. Most UV photodetectors convert photons into carriers, causing the circuit to produce voltage or current changes, thereby converting the detected light signals into electrical signals.

As for photosensitive materials, they can be roughly divided into organic and inorganic materials. Though printable and solution-processed organic semiconductors are widely used in UV photodetectors [8], improving the life of the device has always been a problem. Among the inorganic materials, silicon, as one of the traditional materials for preparing photodetectors, has limited absorption range and weak absorption, and silicon photodetectors need to use expensive filters to resist interference, which increases equipment costs. In addition, the filter may cause visible light leakage after long-term use,



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). thereby reducing the service life of the device. In recent years, due to the advantages of high electron saturation drift speed, high thermal conductivity, and high breakdown strength, wide-band gap semiconductors, including group III nitrides (such as GaN, etc.), SiC, metal oxides (such as TiO₂, ZnO, SnO₂, etc.), and so on, have broad application prospects in UV photodetectors [9,10]. Among the above semiconductors, III-nitrides and SiC are expensive, inflexible, and difficult to prepare in a large area, while metal oxides have attracted a wide range of researchers' interest due to their easy preparation, flexibility, transparency, and printability [11,12]. Table 1 summarizes the development of UV photodetectors of different materials in recent years.

| Structure | Material | Bias (V) | Dark Current | Detectivity (Jones) | Responsivity (A/W) | Response Time (s) | Ref. |
|-----------------------|-------------------------------------|------------------|---------------------------|------------------------|-----------------------|-------------------|------|
| p-i-n | SiC/Si | _ | 10^{-11} A/cm^2 | _ | 0.28 | _ | [13] |
| p-i-n | 4H-SiC | 5 | 2.5 pA/mm ² | — | 0.13 | _ | [14] |
| MSM | Cs ₂ AgInCl ₆ | 5 | 10 pA | $\sim 10^{12}$ | $\sim \! 0.013$ | 0.8 ms/1 ms | [15] |
| MSM | $(PEA)_2PbBr_4$ | 10 | ~0.25 pA | $1.55 	imes 10^{13}$ | ~0.031 | 0.41 ms/0.37 ms | [16] |
| MSM | ZnO | $2	imes 10^{-4}$ | 1.32 pA | $1.45	imes10^{15}$ | 0.014 | 250 s/150 s | [17] |
| pn junction | ZnO-Ga ₂ O ₃ | 0 | ~1 nA | $6.29	imes10^{12}$ | $9.7	imes10^{-3}$ | 0.1 ns/0.9 ns | [18] |
| 3D nano- herojunction | NiO/ZnO | 1 | 18 pA | _ | 13 | 5 s/9 s | [19] |
| pn junction | GaN/Ga ₂ O ₃ | 0 | _ | $1.23	imes10^{11}$ | $5.443	imes10^{-3}$ | 0.1 s/0.08 s | [20] |
| herojunction | SnO_2/GO | 1 | 100 nA | $1.4	imes10^{15}$ | 395 | 120 s/100 s | [21] |
| herojunction | ZnO/GO | 1 | 0.18 µA | $2.6	imes10^{12}$ | ~0.3 | 160 s/190 s | [22] |
| HEMTstack | InAlN/GaN | 5 | < 32 pA | — | 32.9 | 3.6 ms/4.2 ms | [23] |
| FET | ZnO NRs | 5 | _ | — | $2.5	imes10^6$ | — | [24] |

Table 1. The parameters of UV photodetector prepared by different materials.

Among the most popular metal oxide semiconductors used in optoelectronic devices, SnO_2 is considered to be one of the most favorable candidate semiconductors [25]. Intrinsic SnO₂ has a wide band gap at room temperature, is transparent in the visible light region, has a wide range of uses, can be flexible, and has an exciton binding energy of 130 meV, stable and corrosion-resistant, making it an ideal material for preparing UV photodetectors [26]. The existence of defects and dangling bonds in SnO₂ plays an important role in the process of light transmission and light detection [27]. Recent studies have shown that the use of surface defect states to capture weak bounded excitons can generate large ultraviolet exciton gains in SnO₂ nanostructures through the giant oscillator strength effect, and due to the large surface area to volume ratio of SnO₂ nanostructures, the number of surface defects has increased significantly [28,29]. These factors make it possible to prepare high-gain SnO_2 nanostructured UV photodetectors. A UV photodetector with high photocurrent gain based on SnO₂ nanowires was reported by Lin et al, with a gain of up to 8000 [30]. Additionally, it is reported that devices based on graphene oxide (GO) and SnO₂ nano-heterogeneous devices have an ultra-high response rate (395 A/W) and excellent I_{Photo}/I_{Dark} value (2380) in ultraviolet light (312 nm) [21]. In contrast, the performance of UV photodetectors made of SnO_2 thin film is relatively poor [31,32].

According to the dimensionality, SnO₂ materials can be divided into one-dimensional, two-dimensional, and three-dimensional. Among them, one-dimensional nanostructures include nanowires (NWs), nanotubes (NTs), nanobelts (NBs), nanorods (NRs), etc.; two-dimensional structures include nanosheets (NSs), etc.; three-dimensional structures include thin films, microwires (MWs) and so on. Currently, various SnO₂ nanostructures, such as nanowires [33], nanowire arrays [34], nanobelts [35], etc., have been prepared and applied to photodetectors. In view of the slow response speed and poor detectivity faced by SnO₂ UV photodetectors with different device structures have been prepared and constructed to achieve different performance optimizations.

This review mainly focuses on UV photodetectors based on SnO_2 , starting from the basic parameters and structures of the photodetectors, and then discussing the progress of transparent, flexible UV photodetectors in recent years. Finally, the optimization of the performance of SnO_2 UV photodetectors is discussed.

2. The Parameters and Structures of Photodetectors

2.1. Parameters

2.1.1. Dark Current

Dark current refers to the current that exists in the photodetector when there is no incident light. A good photodetector has a large ratio of photocurrent to dark current. Generally, dark current is generated by the following situations [36]: (1) When an ohmic contact is formed between the electrode and the semiconductor layer, there is a potential difference between the electrode and the semiconductor layer, and electrons and holes will move to the positive electrode and the negative electrode, respectively, to form a current; (2) When the metal and the semiconductor are in contact, due to the tunneling effect, the carrier may pass through the barrier and form a current; (3) If the semiconductor is non-uniformly doped, carriers will diffuse from the high-concentration area to the low-concentration area, and so on.

2.1.2. Responsivity

The responsivity (R) refers to the ratio of the photocurrent generated by the device to the incident light power under the excitation of a specific wavelength, and it is also proportional to the external quantum efficiency (EQE), which can be expressed by the formula (1). The responsivity spectrum can be obtained by measuring the photocurrent of the photodetector in a specific spectral range under illumination.

$$R = \frac{I_{ph} - I_{dark}}{P_{light}} = \frac{EQE}{hc/e\lambda'}$$
(1)

where I_{ph} is the photocurrent generated by the device, I_{dark} is the dark current of the device, plight is the power of the incident light, h, c, e, λ are Planck's constant, speed of light, electron charge, and incident wavelength, respectively, and EQE is the external quantum efficiency. The responsivity is usually related to the device structure, material, etc. For example, the gain of an avalanche photodiode will produce a higher responsivity. The external quantum efficiency refers to the ratio of the number of electron–hole pairs collected to the number of incident photons per second. Generally, a photon can only excite a pair of electron–hole pairs, so the EQE will be less than 100%. However, in a special photodetector, when the exciton energy is greater than the band gap value, a photon can excite several electron–hole pairs, and the EQE will be greater than 100% [37,38].

2.1.3. Detectivity

Specific detectivity (D*) represents the smallest optical signal that the device can detect, which is related to the responsivity and noise of the device, and can be expressed by formula (2):

$$D^* = \frac{R\sqrt{AB}}{i_{\text{noise}}},\tag{2}$$

where R is the responsivity, A is the effective area under illumination, B is the detection bandwidth, and i_{noise} is the total noise measured.

2.1.4. Response Time

Response time is another criterion for evaluating the quality of photodetectors. Response time refers to the time required for the output of the detector to respond to changes in the input light intensity, and it consists of two parts: rise time and decay time. In the case of pulses, the rise time refers to the time required for the photodetector output level to change from 10% to 90% of the peak output level, and the decay time refers to the time required for the output level to change from 90% of the peak output level to 10%. The light response curve of a typical photodetector can be fitted using the double exponential relaxation equation (Equation (3)).

$$I = I_0 + C_1 e^{-t/\tau_1} + C_2 e^{-t/\tau_2},$$
(3)

where I_0 is the steady-state current, C_1 and C_2 are constants, τ_1 and τ_2 are the relaxation time constants, and t is the time.

2.1.5. Gain

Gain is another important parameter of photodetectors. Due to the applied bias, the light in the material excites the holes to migrate to the anode, but the electrons are trapped by the defects. Once the holes reach the anode, due to the conservation of charge in the material, the holes will be replenished from the cathode at this time. This process will continue until the holes recombine with the trapped electrons. Therefore, after a single electron–hole photogeneration, multiple holes circulate in the material, resulting in high gain [39]. The gain can be calculated from the measured carrier lifetime and transit time, as shown in Equation (4) [40].

$$Gain = \frac{\tau_{lifetime}}{\tau_{transit}} = \frac{\tau_{lifetime}}{d^2/\mu V},$$
(4)

where τ_{lifetime} is the carrier lifetime, τ_{transit} is the transport time of carriers between electrodes, d is the thickness of the device, μ is carrier mobility, and V is the bias voltage. Compared with EQE, the gain can reach a large value. When the distance between the electrodes is less than the mean free path of carriers, the gain is always greater than 1. High gain means high sensitivity, making the detector suitable for applications such as fiber optic communication receivers, high-resolution imaging, and laser microscopes [41].

2.2. Device Structures

According to the different working mechanism, the device structure of a UV photodetector can be divided into the photoconductive type and photovoltaic type.

The photoconductive UV photodetector is generally composed of electrodes and lightsensitive SnO_2 , as shown in Figure 1a. When light is irradiated, the carrier concentration of SnO_2 in the device will change, which will cause a change in conductivity, and this change will eventually be the output in the form of current. This kind of device structure is easy to prepare and has a low cost, and they usually have a higher gain, but longer response time [42,43], and they also have higher dark current and noise. On the surface of SnO_2 which is generally not modified by other materials, due to the periodic break of the crystal lattice, a large number of dangling bonds are formed, and the surface state of the acceptor type is generated on the surface. Electrons are transferred from the inside to the surface, causing a carrier depletion layer to form near the surface and causing the band to bend. Therefore, the surface will dominate the photocurrent transport in the one-dimensional nanostructure [44,45].

The photovoltaic UV photodetector separates the photogenerated electron–hole pairs by establishing a built-in electric field. The electrons and holes are collected by the cathode and the anode, respectively, which causes the voltage change of the external circuit to achieve the purpose of converting optical signals into electrical signals. As shown in Figure 1b, the built-in electric field can be generated through the contact between n-type and p-type materials. Of course, when the contact between the metal electrode and the n-type SnO₂ material is Schottky contact, the energy band of the SnO₂ semiconductor at the interface will be bent, forming a Schottky barrier, achieving the effect of separating electron–hole pairs [46]. In addition, because the preparation of good p-type materials is relatively difficult, the built-in electric field can also be generated by using two materials with different working functions. This situation is similar to Schottky contact, as shown in Figure 1c.



(c)

Figure 1. (a) SnO₂ nanowire UV detector structure diagram. Reproduced with permission from Ref. [47]; 2011, Wiley; (b) Schematic representation of Al/SnO₂: Si/SnO₂: Ga/ITO heterojunction photodiode [21]; (c) Structure diagram and working mechanism of GNWs/SnO₂ devices under UV light. Reproduced with permission from Ref. [48]; 2019, Elsevier.

3. Transparent SnO₂ UV Photodetector

The optical band gap width of SnO_2 at room temperature is 3.6~4.3 eV. When the energy of photons incident on the SnO_2 material is less than the optical band gap width, most of the photons will pass through. At this time, the SnO_2 material will show good transparency in this waveband. The photon energy value of visible light is 3.1 eV, so SnO_2 material has good transparency in the visible light range (380~780 nm). If matched with other suitable functional layers and substrates, it is possible to realize a transparent UV photodetector.

Among many metal oxides, zinc oxide (ZnO), nickel oxide (NiO) and so on, which have band gaps of 3.3 eV,3.5 eV, etc., have good transparency in visible light range and are often used in UV photodetectors when combined with SnO₂. Based on the electrospinning technology, Tian and his team reported a ZnO/SnO₂ nanofiber UV photodetector with a transparency of up to 90% in the visible light band [49], as shown in Figure 2a. Figure 2b shows the spectral response of the photodetector to different wavelengths and the strong absorption at wavelengths below 350 nm in the light absorption spectrum; for light with a wavelength of more than 400 nm, the responsivity is very low. Although the device has good transparency, the response time is longer, and the rise and decay times are 32.2 s and 7.8 s, respectively, which is similar to the p-SnO₂: Ga/n-Ga₂O₃ nanowire UV photodetector reported by Hsu [50]. This may be since a large number of photogenerated carriers are trapped by defects in the metal oxide and the distance between the electrodes is smaller than the mean free path of the photogenerated carriers, and thus the gain and the response speed are reduced.

The connection structure of the nanostructure heterojunction usually includes: overlapping n-type SnO_2 and p-type material films, crossed n-type and p-type nanofibers, and so on. Compared with the n-SnO₂ nanobelt/p-NiO thin film UV photodetector reported [51] by Long et al., the n-SnO₂-p-NiO nanofiber array (NFA) UV photodetector has a cross-bar structure prepared by the electrospinning method, and the transmittance of the device can reach ~90% in the visible light region, which is mainly due to the pores of the SnO₂-NiO fiber cross-bar structure and the wide band gap of the semiconductor [52]. Under -5 V bias, the highest responsivity of the device occurs at 250 nm, which is close to ~8.67 A/W, and the EQE is calculated to be 4337.17%. The authors believe that this is due to the trap states in p-NiO trapping photo-generated holes and also because the electron mobility in n-SnO₂ is relatively high, so the electrons will circulate in the circuit many times and realize the optical gain effect [53]. The photodetector can also work at 0 V, the photocurrent is 10^{-10} A, and the on-off ratio is about 140, which is expected to be used in automatic force detectors.

Due to the existence of surface states such as surface electron traps and oxygen adsorption, SnO₂ UV photodetectors generally have good sensitivity, but they also limit the further improvement of response speed. This is because these defects act as a recombination center, which traps photo-generated carriers and reduces the efficiency of light detection. At the same time, they are like donor impurities, leading to a huge carrier concentration [54,55], and therefore the photodetectors have a large dark current, hindering the optimization of the response time and photocurrent of the device. The construction of the core–shell structure can modify the surface of SnO₂ and reduce oxygen adsorption and can also construct a heterojunction, generate a built-in electric field to promote the separation of photogenerated electron–hole pairs, and effectively improve the performance of the device.



Figure 2. (a) Optical transmittance of the device in glass; (b) Spectroscopic photoresponse of the device measured at a bias of 5.0 V at different wavelengths ranging from 250 to 630 nm. The inset is optical absorption spectrum. Reproduced with permission from Ref. [49]; 2013, Wiley; (c) Schematic diagram of the structure of SnO_2 -TiO₂ photodetector; (d) Time response of SnO_2 -TiO₂ photodetector under 40 mW/cm² UV light (365 nm) illumination. Reproduced with permission from Ref. [56]; 2014, Elsevier.

A self-powered UV photodetector, that is, a UV photodetector without an external power supply, is not only small in size and light in weight, but also environmentally friendly and energy efficient [57,58], and it is particularly attractive in application environments where power systems are difficult to reach, such as seabed oil spill monitoring, forest fire prevention and control, etc. [59]. Gao et al. used a solution method to grow a layer of SnO₂ nanosheets on a 2.2-mm-thick FTO, then deposited a layer of TiO₂, and finally assembled a photoelectrochemical, self-powered UV photodetector based on the SnO₂-TiO₂ core–shell structure [56]. Compared with the previously reported photodetectors based on nano-TiO₂ film (0.08 s and 0.03 s) [60] and the ZnO/TiO₂ core–shell structure (0.02 s and 0.009 s) [61], the response of the device is faster (0.02 s/0.004 s), as shown in Figure 2d. In addition, the spectral response peak of the SnO₂-TiO₂ core–shell UV photodetector is 0.6 A/W, which is located at 330 nm.

The use of organic-inorganic composite materials to prepare UV photodetectors is a popular direction. There are various reports on the use of suitable organic materials to modify the surface of SnO_2 nanostructured films [62,63], and the purpose is generally to build a PN junction, reduce dark current, and broaden the spectral response range of SnO₂ photodetectors. Among them, graphene is a material that can be applied to photoelectrons and photodetectors [64,65], and the work function of graphene is generally smaller than that of SnO₂, which avoids the generation of electronic barrier regions, so that the transfer of carriers between them produces a synergistic effect [66]. Singh et al. used hydrothermally grown SnO₂ nanowires and reduced graphene oxide (rGO) to prepare a UV photodetector, and the transmittance of the device in the visible light range is only between 30% and 40% [67]. Under the voltage of 3 V, the dark current of the device is only 2 nA, and the photocurrent increased by 2 orders of magnitude compared to the dark current. The work function of GNWs (4.5 eV) [68] is smaller than that of SnO_2 (4.9 eV) [69], and the contact between GNWs and SnO₂ causes the energy band at the interface to be bent, and an electron accumulation layer is generated. When a photo-generated electron-hole pair is generated, it is separated by the built-in electric field, and the photo-generated electron is quickly collected by GNWs, reducing the probability of being trapped by SnO₂ defects. SnO₂ is mainly responsible for the generation of light-generated charges, while GNWs play an important role in the efficient separation and rapid transport of light-generated charges [48]. Although the use of graphene has replaced the role of p-type materials to a certain extent, the UV detection performance of the device has been improved to a certain extent. However, due to the small forbidden band width of graphene, the transparency of such UV photodetectors made of composite materials is generally worse than that of all-metal oxide UV photodetectors.

4. Flexible SnO₂ UV Photodetector

Flexible electronic devices have many potential applications, such as flexible mobile phones, smart fabrics, artificial skins, epidermal electronic products, and other products due to being bendable, foldable, and stretchable. In order to meet people's needs for protection and the monitoring of ultraviolet radiation and the portability of electronic protection products, UV photodetectors are required in complex environments such as human skin, and so the devices are required to be stable and have good durability under deformation. Therefore, it is necessary to prepare a high-performance, flexible UV photodetector.

Flexible substrates generally include polyimide (PI), polyethylene naphthalate (PEN), carbon cloth, etc., and are often selected for sensing applications. With the heterojunction structure of one-dimensional materials, it is difficult to achieve good interface contact and uniform assembly of two one-dimensional nanomaterials due to the limitation of material size. Javey and his team proposed a contact printing method, as shown in Figure 3, which can achieve dense assembly with high uniformity and reproducibility [70]. Based on the contact printing method, Ha et al. prepared a single-walled carbon nanotube (SWCNT)/SnO₂ Nanowire heterojunction on a PI substrate [71]. The I_{ph}/I_{dark} of the device under reverse bias reached 10^4 , indicating that it has a certain application potential in UV



photodetectors. The proposal of this printing method provides a feasible solution for the large-area and uniform preparation of nano-structured UV photodetectors.

Figure 3. Schematic of the process flow for contact printing. Reprinted with permission from [70]. Copyright 2007 American Chemical Society.

Using Au catalysis, Deng et al. deposited a uniform SnO₂ nanoparticle film on a carbon cloth template by atomic layer deposition and obtained SnO₂ nanowire arrays by vapor transport deposition [72]. It can be seen from Figure 4a that the length of these nanowires was about 5 μ m, and they were arranged vertically on the surface of the SnO₂ layer. In the case where no carbon cloth template, SnO₂ nanowire array hierarchy remained intact, as seen in the illustration in Figure 4a since the SnO₂ nanoparticle film enhances the structural stability of the device. The SnO₂ nanoarray was transferred to the SiO_2/Si substrate, and then Au/Ti electrodes were deposited to form a UV photodetector. Figure 4b shows the spectral response of the photodetector under a constant light intensity of 1.0 V bias. The device had an obvious photocurrent in the ultraviolet region. The cut-off wavelength was \sim 350 nm, and the responsivity was maximized at \sim 250 nm. Figure 4c shows the I-V curve of the photodetector under different wavelengths and dark conditions. Under a bias voltage of 1.0 V, the dark current of the device was only 2.3 pA, and the photocurrent can reach 0.5 nA irradiated the light of 350 nm. It is generally believed that oxygen molecules adsorb to the surface of SnO_2 and trap free electrons, thereby forming a low-conductivity depletion layer on the surface area. Under UV irradiation, light excites holes to migrate to the surface, and through electron-hole recombination, the electro-adsorbed oxygen ions (negatively charged) are decomposed, resulting in enhanced conductivity [73–76]. Figure 4d plots the time–response curve of the photodetector. It can be seen that the rise time and decay time were both less than 0.3 s. Such a fast response may be due to the formation of a large number of nanowire/nanowire connections in the nanostructure, which form the Schottky connection and the conduction path of electrons [77].

In flexible electronic products, unlike bendability, achieving superior stretchability is more challenging. Kim et al. reported an active stretchable SnO₂ nanowire ultraviolet sensor array with an observed average photosensitivity (I_{UV}/I_{dark}) of 10⁵ under low-power UV light (0.03 mW/cm²) and a gate bias of -40 V [78]. The I_{dd} -time curve was tested under $V_{dd} = 1$ V and $V_{data} = 0$ V, and the results show that the photocurrent was saturated within 40 s. When the UV light was turned off, the recovery time was estimated to be 10 s. Moreover, the pre-strain of up to 23% caused by the radial deformation of the device did not degrade the performance.

1.5x10⁻² hv 3 Responsivity (a.u.) 1.0x10⁻² Au/T SiO, Si 5.0x10 0.0 30un 400 600 300 500 Wavelength (nm) (a) (b) 0.6 (c) 120 ON ON ON ON 0.4 100 0.0 Current (nA) 0.0-0.2 80 Current(nA) 60 dark 40 550nm 20 450nm -0.4 350nm OFF OFF OFF OFF OFF 0 -0.6 -1.0 1.0 0 100 200 300 400 -0.5 0.0 0.5 Voltage (V) Time (s) (d) (c)

Figure 4. (a) Cross-sectional SEM image of 3D SnO₂ nano array; (b) Spectral response of the device; (c) I-V curves under different wavelengths and dark conditions; (d) Time–response curve of the device. Reprinted with permission from [72]. Copyright 2013 American Chemical Society.

In order to achieve good tensile properties, the structure of SnO_2 nanomaterials is a good starting point. Huang et al. prepared SnO2 nanowebs with "spring" and "wave"like geometries by electrospinning, as shown in Figure 5a, and realized the preparation of a UV photodetector with superior stretchability on a polydimethylsiloxane (PDMS) substrate [79]. Experiments have shown that SnO_2 nanowebs without pre-strain can be stretched to 70%, and under 100% pre-strain, SnO2 nanowebs can withstand up to 160% tensile strain, and the resistance (R/R_0) is only 3.1. As shown in Figure 5b, SnO₂ nanowebs still maintained their structural integrity and electrical continuity after 1000 cycles at a tensile strain of 30%. This excellent tensile performance can be attributed to the excellent bendability brought by the unique geometric structure of SnO₂ nanowebs, and the finite element simulation results also show that bulked nanobelts can withstand large reversible strains during tension or compression. The device could be placed on the finger joint to simulate the use environment of the wearable product, as shown in Figure 5c. The device exhibits a reversible change in resistance during repeated bending cycles, and the electrical conductivity does not significantly attenuate, showing its good mechanical presence and durability. At the same time, the rise and decay times of the device in the bending and straightening state are both 12 s and 18 s, and the response speed is almost negligible due to the deformation.



(c)

Figure 5. (a) SEM images of pre-strained SnO_2 nanowebs, showing spring- (upper and lower left) and wave-like geometries (lower right); (b) R/R0 of the SnO_2 nanobelt network on 100% pre-strained PDMS as a function of stretching cycles; (c) Repeated finger bending test of wearable SnO_2 photodetectors. Reproduced with permission from Ref. [79]; 2015, Wiley.

The density of defects in SnO₂ is difficult to control, which makes it difficult for the electrical characteristics of SnO₂ to meet the requirements of devices. Doping can effectively overcome this problem, so as to realize the adjustment of its electrical and optical characteristics [80]. Shahid et al. reported a flexible and transparent Pt/In-SnO₂ nanobelt/Pt UV light photodetector based on an In-doped SnO₂ nanobelt [81]. When the doping concentration is 3 wt.%, the dark current is 4.7 nA, the photocurrent is 49.6 μ A under the irradiation of light with a wavelength of 254 nm and a density of 0.97 mW/cm², and the highest light sensitivity is $\sim 10^4$, while the light sensitivity of pure SnO₂ nanobelt is estimated to be only about \sim 143. If the diameter of the crystal grain is equivalent to 2 times Debye length, then high sensitivity can be obtained, because the carriers will be localized on the surface of the nanomaterial, and the surface carriers can be captured by the dopant [82]. Additionally, the Debye length of SnO_2 is about 3.07 nm according to calculations. Compared with the un-doped SnO₂ nanoribbons with a grain size of 10.5 nm, the crystal grain size of the SnO₂ nanobelts doped with 3 wt.% In³⁺ is reduced to 5.6 nm, which may be the reason for the increased photosensitivity of SnO_2 nanobelts. In addition, the increase in photosensitivity can also be attributed to the decrease of the electron balance density by doping In^{3+} in SnO₂, which leads to an increase in oxygen adsorption on the surface of the nanobelt.

In addition, the author also tested the flexibility of the device. When the strain increased from 0% to 0.625%, the photocurrent of the device decreased very little. Moreover, when the strain increased to 1.66 strain%, compared with 0% strain, the photocurrent was only reduced by about 45%. In addition, after the device was bent to a radius of 8 mm (0.83% strain) for 300 bending cycles, the conductivity and response speed were less affected, showing excellent stability.

| Material | Transparency (380–780 nm) | Flexible/Substrate | Dark Current | Responsivity (A/W) | Response Time | Ref. |
|--------------------------------------|------------------------------|---------------------|--------------|-----------------------|---------------|------|
| ZnO/SnO ₂ NFs | >80% | _ | 1.7 pA | _ | 32.2 s/7.8 s | [49] |
| SnO ₂ NBs/NiO | >60% | _ | _ | _ | 17 s/9 s | [51] |
| SnO ₂ -NiO NFs | >85% | _ | _ | 8.67 | 8 s/— | [52] |
| SnO ₂ NS-TiO ₂ | >60% | — | — | 0.6 | 20 ms/4 ms | [56] |
| SnO ₂ NW/rGO | >30% | _ | 2 nA | _ | _ | [67] |
| SWCNT/SnO ₂ NW | _ | PI substrate | _ | _ | _ | [71] |
| SnO ₂ NWAs | _ | carbon cloth | 2.3 pA | _ | < 0.3 s | [72] |
| SnO ₂ NW device array | _ | 23% pre-strain | 2 pA | _ | 40 s/10 s | [78] |
| SnO_2 nanowebs | >70% | 160% tensile strain | _ | _ | 12 s/18 s | [79] |
| In-SnO ₂ NB | — | 0.83% strain | 4.7 nA | _ | —/<0.175 s | [81] |

Table 2. Comparison of the parameters of various photodetectors.

5. Optimization

todetectors.

To realize a flexible and transparent UV photodetector based on SnO_2 , one firstly needs to prepare a high-performance SnO_2 UV photodetector. Compared with other popular metal oxide materials for preparing UV photodetectors, the surface of SnO_2 has more defect states, which makes it easier for UV photodetectors based on SnO_2 materials to obtain higher gains, but this also means that the optimization of parameters such as dark current and response time will be more difficult. Although methods such as improving crystallinity and constructing a core–shell structure have been adopted to prepare UV photodetectors with superior performance, further improvements are still needed to overcome more complex and diverse application environments.

Table 2 summarizes the research progress of transparent and flexible SnO₂ UV pho-

The defects in SnO₂ are mainly oxygen vacancies and lattice defects which are difficult to control, and research has found that doping can effectively solve these problems. On the one hand, the introduction of excess impurities can improve the crystallinity of SnO₂, reduce the scattering effect, affect the size of the crystal grains, and thus have a positive impact on the UV response of the device [83]. According to previous reports, introducing Zr^{4+} as a dopant can control the crystallinity of SnO₂ [84]. When the Zr^{4+} doping content changes from 0 at.% to 3 at.%, the SnO₂ grain size can increase from 10.213 nm to 11.315 nm; however, when the doping content continues to increase to 10 at.%, the crystallinity of SnO₂ becomes worse, and the grain size decreases to 8.644 nm. On the other hand, the selection of appropriate dopants can achieve the suppression of oxygen vacancies, further reduce the dark current of the device, and increase the gain of the device. The main requirements for this dopant are as follows [85,86]: the bonding strength of the doping element and oxygen should be higher than the bonding strength of tin and oxygen; the size of the dopant should be smaller than the tin ion; and the high Lewis acid strength should be higher.

In order to solve the problem of a slow response time, the UV photodetector with a PN structure has attracted wide attention. Among them is the use of the core–shell structure, which not only optimizes the response speed of SnO₂ UV photodetectors, but also is expected to be applied to self-powered devices to expand the application environment of SnO₂ UV photodetectors. At present, Au, etc. materials are usually used as electrodes [87] in order to build Schottky SnO₂ UV photodetectors. Generally, the contact between the two metal electrodes of the Schottky detector and the semiconductor layer can be divided into an ohmic contact side and a Schottky contact side. A built-in electric field (depletion region) is formed at the interface of Schottky contact, which can also enable the photogenerated carriers to be effectively separated on the interface. Moreover, Schottky-type devices generally do not require a p-type semiconductor functional layer, thus avoiding the influence of interface defect states caused by the mismatch of the n-type layer and the p-type layer material lattice, thermal expansion coefficient, etc., which is beneficial to reduce

the probability of photo-generated carriers being captured, and the mobility of photogenerated carriers at the interface of the device is improved, thereby increasing the rate at which the photo-generated carriers are collected by the electrode, so that the response time is improved. Therefore, in theory, a UV detector based on the Schottky structure could also improve the response speed of the device. However, there are relatively few reports on Schottky contacts, which may be due to fewer electrodes with suitable metals and alloys.

The combination of organic–inorganic materials has always been a hot research field. The application of this hybrid structure is expected to combine the advantages of inorganic semiconductors and organic polymer semiconductors, integrating high electron mobility, good p-type conductivity, and low-cost solution processing, making mass production possible [88]. SnO₂ nanomaterials can be modified with organics to achieve surface modification of SnO₂ and reduce band bending caused by oxygen adsorption; it can also be prepared from organics, such as water–oil interface assembly [89], etc., to reduce preparation costs.

In recent years, surface plasmon (SP) has been considered to be one of the effective methods to improve the sensitivity of semiconductor-based UV photodetectors [90]. The principle is that when the resonance wavelength of the surface plasmon is consistent with the response wavelength of the UV detector, coupling oscillation will occur, and the spectral response will increase significantly. Metal nanoparticles such as aluminum and silver can be selected as plasma to be deposited on the top of the device. However, there are few studies on the application of surface plasmons to UV photodetectors, and further research is needed on the mechanism, repeatability, and assembly of surface plasmons.

In terms of preparation methods, most of the current methods for preparing SnO_2 UV photodetectors use atomic layer deposition, electrospinning, hydrothermal methods, etc. [47,87,91], which are relatively difficult to apply to large-area uniform preparation. With the maturity of inkjet printing technology, its advantages such as precise patterning and large-area preparation have aroused the interest of many scholars, and there are more and more reports on inkjet printing SnO_2 sensors [92–94]. However, the main difficulties at present mostly involve preparing suitable printable inks and lowering the sintering temperature. For inkjet printing technology, it is crucially important to adjust the ink viscosity, surface tension and other characteristics to meet the requirements of printing equipment, and in most cases, it is necessary to use suitable additives to solve the problem of uneven film, so that the printed film has good uniformity. Studies have shown that if general annealing technologies, such as hot stage annealing, etc., are used to remove organic matter and other impurities in the film prepared by the solution methods, SnO₂ annealing at 350 °C and below is generally amorphous. If the better crystallinity is required, the annealing temperature must be greater than 350 °C, or even 500 °C and above [95,96]. However, the glass transition temperature of flexible plastic substrates is generally less than 400 °C [97]. For example, the glass transition temperatures of commonly used polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and polyimide (PI) are 80 °C, 120 °C, and 360 °C~400°C, respectively. By lowering the sintering temperature to adapt to the flexible substrate, it is possible to expand the application of SnO₂ ultraviolet photodetectors prepared by inkjet printing in flexible electronic devices.

6. Summary

In this review, the concept and understanding of the basic parameters of photodetectors are reviewed, and the operating mechanism of SnO_2 UV photodetectors and various influencing factors are discussed. The research progress of UV photodetectors based on transparent and flexible SnO_2 is summarized, which provides key insights for the further development of SnO_2 UV photodetectors in flexible electronic products. SnO_2 has many excellent characteristics, such as excellent stability and transparency, low material cost, etc., and is also often used in various optoelectronic devices. However, there are relatively few studies on the application of SnO_2 materials in UV photodetectors, and it is hoped that this review will stimulate the research on SnO_2 materials. **Author Contributions:** Funding acquisition, H.N., R.Y., J.P., and Z.X.; resources, J.P. and X.L.; investigation, Q.Y. and X.Z.; data curation, Q.Y., W.Z., and C.G.; writing—original draft preparation, Q.Y. and X.Z.; writing—review and editing, H.N., R.Y., and D.L.; project administration, Z.X. and R.Y. All authors have read and agreed to the published version of the manuscript.

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