TOPICAL REVIEW — ZnO-related materials and devices

One-dimensional ZnO nanostructure-based optoelectronics*

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Semiconductor nanowires, with their unique capability to bridge the nanoscopic and macroscopic worlds, have been demonstrated to have potential applications in energy conversion, electronics, optoelectronics, and biosensing devices. One-dimensional (1D) ZnO nanostructures, with coupled semiconducting and piezoelectric properties, have been extensively investigated and widely used to fabricate nanoscale optoelectronic devices. In this article, we review recent developments in 1D ZnO nanostructure based photodetectors and device performance enhancement by strain engineering piezoelectric polarization and interface modulation. The emphasis is on a fundamental understanding of electrical and optical phenomena, interfacial and contact behaviors, and device characteristics. Finally, the prospects of 1D ZnO nanostructure devices and new challenges are proposed.

Keywords: one-dimensional ZnO optoelectronics, self-powered photodetector, strain engineering, Van der Waals heterostructure

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1. Introduction

The rapid advances in micro/nanotechnology nowadays will gradually shift focus from demonstrating discrete devices to developing integrated systems of a certain complexity.[1] One-dimensional (1D) semiconductor nanostructures can serve as one of the most powerful building blocks for multi-functional integrated systems, with large surface-to-volume ratios, high crystallinity a direct pathway for electron transfer, and ease of integration with microelectronic technologies.[2–4] Among the known oxide semiconductors, ZnO is a promising material for short-wavelength optoelectronic devices such as photodetectors, light-emitting diodes, and laser diodes, not only because of its superior semiconducting properties, with a direct wide band-gap (3.37 eV) and a large exciton binding energy (60 meV),[5–9] but also due to its unique piezoelectric properties.[10,11] ZnO nanowire (NW)-based optoelectronic devices have been widely investigated and their performance has been remarkably improved by strain-induced piezoelectric polarization. Moreover, international interest in ZnO materials has extended to solar photovoltaic energy conversion,[12–14] because they can be obtained in a wide variety of nanostructures by low-cost processing techniques: nanoparticles, nanowires, nanoflowers, nanosheets, and nanoarrays.[15–20] In this paper, we review recent developments in photodetectors that utilize 1D ZnO nano-materials mainly nanowires and nanowire arrays as well as new designs for device fabrication and some effective approaches for performance enhancement such as optimizing the material and device geometry, semiconductor band-structure engineering with piezoelectric polarization, and interface modulation. Further, we focus on a deeper understanding of experimental observations of electrical and optical phenomena, interfacial and contact behaviors, and device characteristics. The outstanding challenges and opportunities for future work are also proposed.

2. One-dimensional ZnO-based optoelectronics

Photodetectors that convert optical signals into electrical ones have wide applications in binary switches used in imaging, light-wave communication, memory storage, and optoelectronic circuits.[21] The ultraviolet (UV) radiation emitted by the sun falls in the range 200–400 nm. Most UV-C (200–290 nm) light and UV-B (290–320 nm) light can be absorbed by the molecules in sunscreen lotions and in the Earth's at-

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mosphere, and UV-A (320–400 nm) light reaching the earth's surface can lead to skin cancer. ZnO, with a direct wide band-gap (3.37 eV) and a large exciton binding energy (60 meV), is the most important material for UV-A light photodetectors. According to the working principle, there are mainly three types of UV detectors based on ZnO: photoconductive,[22] p–n junction,[23,24] and Schottky-barrier.[25]

There are four key parameters to evaluate ZnO-based UV photodetector performance. (i) Sensitivity (S) is the ratio of photocurrent ($I_{\rm ph}$) to dark current ($I_{\rm dark}$). (ii) Responsivity (R) of the photodetector is determined by the ratio of electrical output signal to incident radiation power ($P_{\rm opt}$), indicating how many photogenerated electron–hole pairs are used to generate the photocurrent, which can be expressed as[26]

$$R = \frac{I_{\rm ph}}{P_{\rm opt}}. \tag{1}$$

(iii) Quantum efficiency (η) is used to estimate photoelectric conversion efficiency that is all photons absorbed contribute to the photocurrent, and can be defined as

$$\eta = \frac{Rh\upsilon}{q}, \tag{2}$$

where h is Planck's constant, ν is the frequency of the incident light, and q is the elementary charge. (iv) Rise time is the time taken by a photodetector to reach $(1-1/{\rm e})$ maximum photocurrent from dark current, and reset time is the time taken to reach $1/{\rm e}$ of the maximum photocurrent.

Due to the large surface-to-volume ratios, photodetectors based on 1D semiconducting nanomaterials usually have high internal gain[27] and superior optical absorption. Also, monocrystalline 1D nanostructures provide direct electrical pathways for rapid charge transport, which benefits the response speed.[28] Currently, due to their simple structural configuration, well-defined growth method and a unique advantage of controllability of the nanostructure,[29] 1D ZnO nanostructures are extensively investigated and widely used to fabricate nano-scale UV photodetectors. In this section, we present the recent developments in photodetectors with external source (requiring an external electric field) and self-powered photodetectors, along with emphasis on efforts to improve the performance of the devices, such as strain enhancement.

2.1. Photodetectors with external sources

The photoconductive detector is essentially a photoconductive resistor. When semiconductors absorb photons of energy larger than the band-gap, a lot of electron–hole pairs are generated, increasing the conductivity of the photodetectors. 1D ZnO nanomaterial-based photoconductors have been investigated in detail by a number of groups. Soci *et al.* reported fabrication and characterization of ZnO nanowire visible-blind UV photodetectors with internal photoconductive gain as high as $G \sim 10^8$. They attributed the high photoconductive gain to oxygen-related hole-trap states at the NW surface, which prevent charge-carrier recombination and prolong photo carrier lifetime, as evidenced by the sensitivity of the photocurrent to ambient conditions.[27] Hu *et al.* developed a novel 1D-semiconductor/1D-semiconductor nanocomposite-based photodetector from highly crystallized ZnS/ZnO biaxial nanobelts. The optimized performance of such photodetectors is much better than that of pure ZnS or ZnO nanostructures or nanoparticle-coated ZnO composites combining high sensitivity, high EQE value, and fast response.[30]

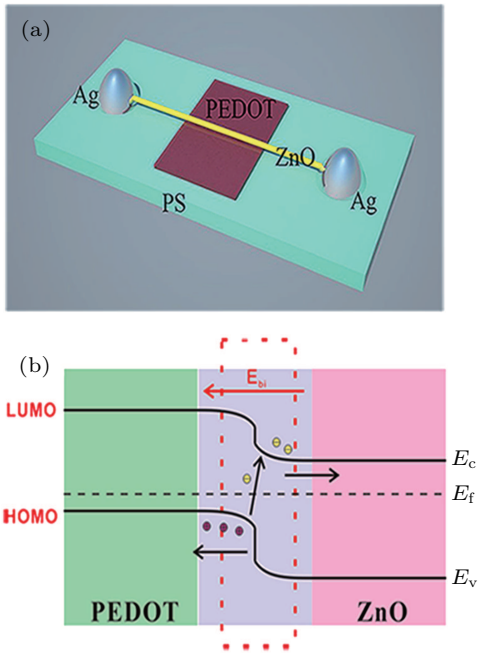


Fig. 1. (color online) (a) Schematic of the N-channel FET detector. (b) Schematic illustration of the electron–hole generation process and transmission process of PEDOT:PSS.

The high photoconductive gain of photoconductive type PDs is attributed to the presence of oxygen-related hole-trap states at the NW surface, which prevent charge-carrier recombination and prolong photocarrier lifetime.[31] Nevertheless oxygen molecule adsorption-desorption is slow, resulting in a long response time. To shorten the response time, an FET detector with a PEDOT: PSS/ZnO wire junction as the gate has been fabricated and investigated. The sensitivity of the junction FET was superior by two orders of magnitude with a fast response time of <1 s at 3 V compared with an Ag–ZnO–Ag detector under illumination of UV light (325 nm). Such a great improvement in photoresponse is attributed to the introduction of a depletion layer, resulting in lower dark current. A physical model based on band energy theory meant to account for the origin of the enhanced performance for FET-PDs has been developed, as illustrated in Fig. 1. To further confirm the

scaling effect of the depletion channel on the performance improvement, representative photoresponse curves with increasing power were measured from 0.17 mW to 17.4 mW at 5 V. The results show that the junction FET channel linearly broadens with an increase of light intensity according to the carrier diffusion theory and the ideal *I–V* characteristics of JFET depletion mode.[32]

Compared with photoconductive photodetectors, a Schottky photodiode has many advantages in the aspects of high quantum efficiency, high response speed, low dark current, high UV/visible contrast, and possible zero-bias operation.[33] Zhou *et al.* reported that by utilizing Schottky contacts instead of ohmic contacts in device fabrication, the UV sensitivity of a nanosensor was improved by four orders of magnitude, and the reset time was drastically reduced from ~ 417 s to ~ 0.8 s.[34] Das *et al.* demonstrated the UV response of a ZnO single NW-based device with ohmic contacts on both sides and Schottky contact on one side. Upon UV excitation, the ZnO nanowire with a Schottky contact exhibited a much faster response (1 s) than the single nanowire detector (20 s) with ohmic contacts.[35] Cheng *et al.* fabricated a UV photodetector of ZnO nanowire Schottky barrier with high photocurrent gain of 4×10^5 and large responsivity of 2.6×10^3 A/W. Also, the recovery time was reduced to 0.28 s when the photocurrent decreased by 3 orders of magnitude. The exponential-type dependence of photocurrent on $N_{\mathrm{SB-interf}}$ and the faster relaxation speed of holes that stayed in the Schottky barrier interface are the physical basis for the fast recovery of the photocurrent.[36]

ZnO nanotetrapods have been utilized to construct many types of prototypical devices such as photoelectric sensors, due to their novel structure with an occupied 3D tetrahedral space. Xie *et al.* investigated the photoluminescence and waveguide behaviors of a single tetrapod by introducing UV light to one of the legs; the resulting PL light can be coupled into the excited leg and guided to the other legs.[37] Research interests of Zhang *et al.* also include single ZnO nanotetrapod-based devices and a lot of our work is focused on improving the device performance by tuning the transport properties of ZnO nanotertrapods.[38] To monitor UV irradiation in ZnO nanotetrapod-based sensors, localized UV irradiation was introduced to the gate leg of a tetrapod and monitored by recording the sensor's current response in real time (see Fig. 2). The results indicate that for both ohmic- and Schottky-contact sensors, localized UV irradiation can be readily monitored by recording the sensor's current responses The sensor's sensitivity alters with strengthened UV light power density, which is observed to be completely repeatable and reversible. It is further proven by the experimental outcome that sensors with Schottky contact characteristic are a better candidate for applications in monitoring localized irradiation. Explanations are given from electron transfer effect and energy band structure respectively.[39]

In contrast to Schottky type photodetectors, p–n type photodetectors have a number of virtues such as low working voltage bias and compatibility with the conventional semiconductor process. However, due to the instability and uncontrollability of p-type ZnO materials, many different p-type semiconductors were used to construct p–n heterojunction photodetectors. Owing to low cost and widely used integrated circuit technology, the silicon wafer has drawn much attention for

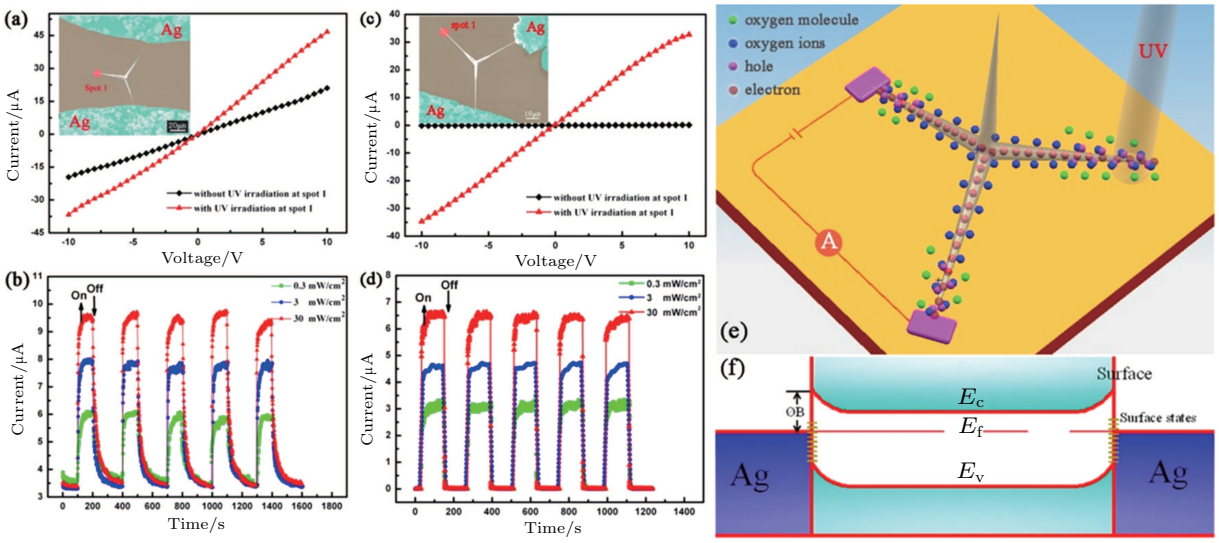


Fig. 2. (color online) (a) *I–V* characteristics with and without localized UV irradiation for ohmic-typed sensor. (b) Current as a function of time recorded at a fixed voltage of 2 V under localized periodic UV irradiation at different power densities for ohmic-typed sensor. (c) *I–V* characteristics with and without localized UV irradiation for Schottky-type sensor. (d) Current as a function of time recorded at a fixed voltage of 2 V under periodic UV light irradiation at different power densities for Schottky-typed sensor. (e) Schematic diagram of the mechanism for sensor response to localized UV irradiation at the third leg of a tetrapod. (f) Schematic energy band diagram of the surface potential of ZnO for sensor with a Schottky contact.

ZnO p–n heterojunction photodetectors. Park *et al.* obtained a wide-range spectral responsivity curve for an n-ZnO/p-Si photodiode fully isolated by ion-beam treatment, which showed a maximum quantum efficiency of 70% at 650 nm and a minimum of 10% at 420 nm.[40] However, compared with the background signal, UV selectivity was relatively low because of the contribution of the electrons generated from silicon's response to visible light. In 2011, Kim *et al.* demonstrated that the UV photodetector properties can be significantly improved by inserting an ultra-thin insulating MgO layer between the n-ZnO nanowires and the n-Si substrate. The photoresponse spectrum revealed good visible-blind UV detectivity with a sharp cutoff at 378 nm and a high UV/visible rejection ratio.[41] In recent years, considerable interest has also arisen for the fabrication of ZnO/organic heterostructures for solar cells, photodiodes and photoelectrochemical applications. Lin *et al.* proposed a near-ultraviolet photodetector based on a ZnO nanowire/polyfluorene hybrid formed by solution processes at low temperature. The relative quantum efficiency of the hybrid device exhibits a nearly three order of magnitude superiority while illuminated under either UV or visible light.[42] Gong *et al.* reported that the depletion zone thickness of the p–n junction between an n-type ZnO and a p-type polyaniline could be controlled by UV and visible light illumination. The photocurrent of the sensor decreases when exposing the photoresponsive sensor to UV light. Meanwhile, the sensitivity and the selectivity of the sensor to light with different wavelengths were realized by surface modifications using PSS and dye, respectively.[43]

2.2. Self-powered photodetectors

Traditional photodetectors (PDs) need an external electric field to drive the photo-generated carriers to generate photocurrent. A self-powered PD based on the photovoltaic effect can operate at zero bias without external power, which is highly desirable to meet the demands of the low-carbon age. When UV light with photon energy larger than the band gap of ZnO is irradiated on the self-powered PDs, electron–hole pairs will be photo-generated. Then the photon-induced electrons and holes are quickly swept away from the built-in electric field in opposite directions, resulting in a photocurrent. For charge separation at the interface, self-powered PDs have three structure types: p–n junction, Schottky junction, and photoelectrochemical.

Junctions between p-type and n-type semiconductors provide the driving force to separate photo-generated electrons and holes. In fact, p–n junction type photodetectors with no external power source have already been reported by many groups. For example, Zhang's group fabricated a single ZnO nanowire/Si film heterostructure PD that showed an ultrafast response of 7.4 ms and a high sensitivity of 2×10^4 for UV light and 5×10^3 for visible light (Fig. 3). The fabricated UV-visible PD was driven by the photovoltaic effect and could output a maximum power of 1.7 nW under 325 nm irradiation and 0.5 nW under 514 nm irradiation. The short circuit current and open circuit voltage showed square root and logarithmical dependencies on light intensity, respectively.[44] Bie and co-workers fabricated a single n-type ZnO nanowire/p-type GaN film heterojunction for application in self-powered UV detectors. The self-powered visible-blind UV detectors have an ultra-fast rise time ($\sim$ 20 μs) and decay time ($\sim$ 219 μs), two orders of magnitude faster than ZnO photoconductivity based photodetectors. The UV detectors were driven by the photovoltaic effect of the ZnO/GaN p–n junction with a short circuit current density of up to $\sim 5 \times 10^4$ mA/cm^{-2}, an open-circuit voltage of $\sim$ 2.7 V, and a maximum output power of $\sim$ 1.1 μW. In addition, a multi-wavelength photodetector was fabricated by integrating the PV device with a CdSe nanowire red-light detector. The integrated nano-circuit functioned as an optical and logic gate and operational multi-state output was also demonstrated.[45] However, considering the large incident laser-power density of $\sim$ 380 μW/μm^2 and low output photocurrent of $\sim 10^{-6}$ A at zero bias, a simple nanoscale junction is far from capable of controlling directional movement of photo-induced electrons and holes. In this case, Hatch *et al.* used an n-type ZnO nanorod array and p-type CuSCN to form a p–n heterostructure as a self-powered UV detector that operated at a nominal zero-applied field, with a photocurrent response of 4.5 μA for a low UV irradiance of 6.0 mW/cm^2. A fast 500 ns rise and a 6.7 μs decay time were recorded with a UV-vis rejection ratio of $\sim$ 100. As a binary UV-detector, working at an applied positive bias of 0.1 mV, a rapid detection time of 4 ns was possible.[46]

In addition, photovoltaic effects usually can be observed in Schottky junction-based devices, which can provide energy for themselves in applications of PDs. This feature makes it possible to detect light irradiation without an external power source. Zhang's group fabricated and investigated proto-devices based on a single ZnO nanobelt. The single Sb-doped ZnO nanobelt bridging an ohmic contact and a Schottky contact can act as a self-powered PD with photoresponse sensitivity of 2200% and a response time of less than 100 ms at zero bias. The performance of the device was found to degrade with decreasing Sb doping concentration (see Fig. 4). The mechanism of the device was suggested to be associated with a suppression of recombination rate of the photo-generated electron–hole pairs in the Schottky barrier and reduced electrical resistivity of the nanobelt due to Sb doping.[47] Also, Zhang and co-workers presented a self-powered photodetector based on a CdS:Ga nanoribbons/Au Schottky barrier diode. Photoconductive analysis revealed that the SBDs were highly sensitive to light illumination with very good stability, reproducibility and fast response speeds

at zero bias voltage. The corresponding rise/fall times of 95/290 ms represent the best values obtained for CdS-based nano-photodetectors.[48] Graphene has been used to replace indium titanium oxide as the flexible transparent conductive electrode for organic photovoltaics, since ITO has the drawbacks of high-cost, limited usability on flexible substrates, and degradation of device performance over time due to indium diffusion. Jin *et al.* fabricated self-powered photodetectors based on CdSe nanobelt/grapheme Schottky junctions. Under zero bias, such a photodetector typically shows high photosensitivity ($\sim 3.5 \times 10^5$) to above-band-gap irradiation (> 1.75 eV at room temperature) and a fast response (with response and recovery times of 82 ms and 179 ms, respectively) in a wide range of switching frequencies (up to 1000 Hz). The photoconductive gain is 28, greater than unity.[49] Furthermore, UV PDs based on integrated ZnO nanowires have also been studied as self-powered PDs. For example, Zhang and co-workers observed that ZnO nanowire array UV PDs with Pt Schottky contacts exhibited self-powered performance. It was also found that this PD had a high sensitivity of 475 without external bias. This phenomenon could be explained by the asymmetric Schottky barrier height at the two ends causing different separation efficiency of photo-generated electron–hole pairs, resulting in photocurrent.[50] In addition, ambient temperature is the key factor that must be taken into account in applications of self-powered PDs in long-term unattended monitoring of a harsh environment. So we researched the effect of temperature on the self-powering properties of UV PDs based on selectively grown ZnO nanowire arrays with Al–Pt interdigitated electrodes. At zero bias, the fabricated photodetector exhibited high sensitivity and excellent selectivity to UV light illumination with a fast response of 81 ms. By tuning the Schottky barrier height through thermally induced variation of the interfacechemisorbed oxygen, an ultrahigh sensitivity of 3.1×10^4 was achieved at 340 K without an external power source, which was 82% higher than that obtained at room temperature. The changes in the photocurrent of the PD at zero bias with various system temperatures were calculated according to thermionic emission-diffusion theory and solar cell theory, and agreed well with the experimental data.[51]

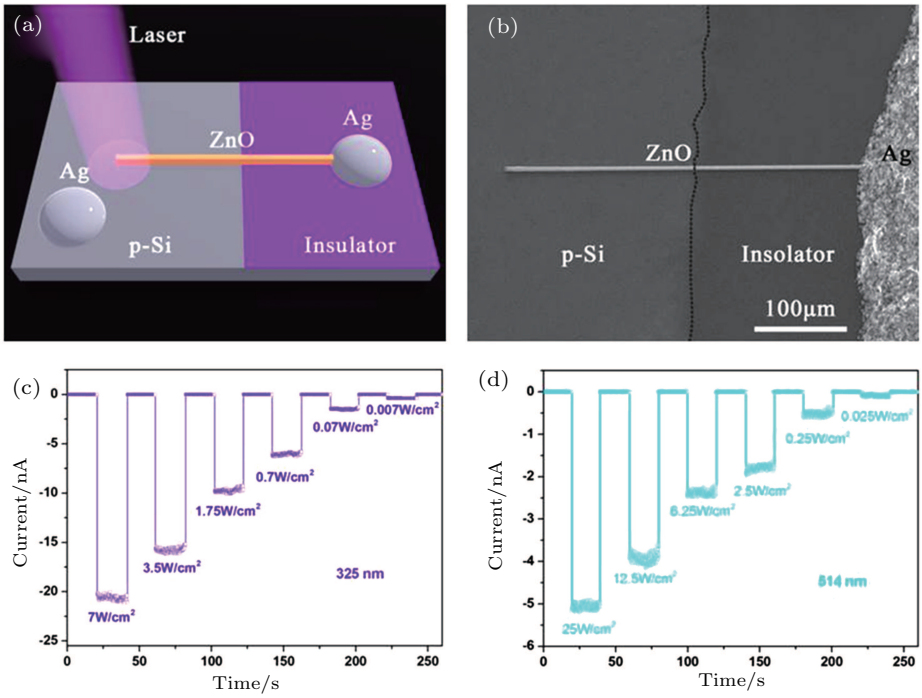


Fig. 3. (color online) Schematic (a) and SEM image (b) of a self-powered PDa single ZnO nanowire/Si heterojunction, and the corresponding photocurrent vs. time curves under UV light illumination (c) and visible light illumination (d).

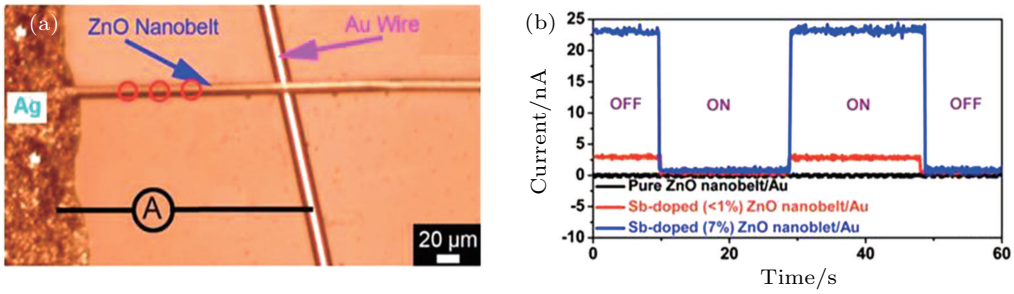


Fig. 4. (color online) (a)Schematic of a self-powered PD based on a single Sb-doped ZnO nanobelt, and (b) photoresponse as a function of time at zero bias.

Recently, photoelectrochemical cells (PECCs) that have the same structure as the conventional DSSCs but without dye adsorption obtain much attention due to their considerable photovoltaic effect under light illumination. Li *et al.* demonstrated the application of a PECC as a self-powered UV-photodetector for detecting UV light. The intensity of UV light was quantified using the output short-circuit photocurrent of the PECC without a power source. This self-powered UV-photodetector exhibited a high photoresponse sensitivity of 269850%, rise time of 0.08 s and decay time of 0.03 s for short-circuit photocurrent.[52]

2.3. Perspectives

Mixed-dimensional van der Waals heterostructure (vdWH) is a new type of heterostructure combining a two-dimensional (2D) component with n ($n = 0, 1, 3$) dimensional (nD) materials. Due to the absence of dangling bonds on the surface of 2D materials, mixed-dimensional vdWHs allow free integration of materials to create brand new devices with diverse functions while ignoring lattice matching. Owing to the wider range of material options, mixed-dimensional vdWHs provide greater freedom in device construction, with advantages in matching complementary properties and in opportunities to control carrier behavior at atomic scale. Mixed-dimensional vdWH photodetectors work mainly by two principles: photovoltage and photogating. In the photovoltage model, photocurrent originates from efficient separation of photocarriers driven by built-in potential. A graphene/ZnO nanorod array heterostructure photovoltaic photodetector was demonstrated by Luo's and Yu's group,[53] as shown in Fig. 5(a). Graphene is selected due to its wide-band transparency and high carrier transport ability. The device showed responsivity of 113 A/W and response speed in milliseconds, owing to formation of a significant Schottky barrier in the device interface. Besides, incident light tends to be trapped by the periodically arranged nanorods array, which enhanced the photoelectric conversion efficiency.

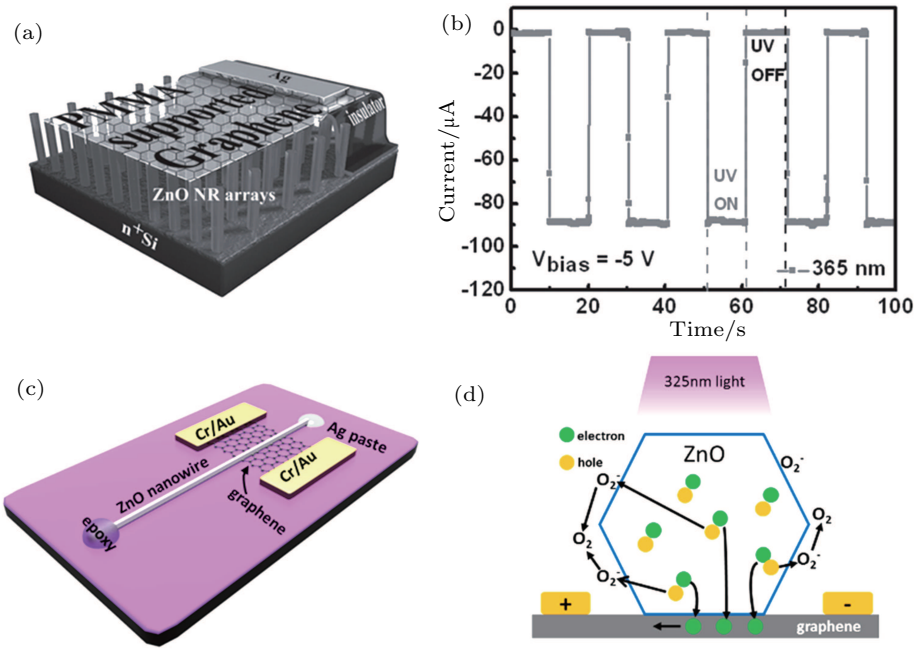


Fig. 5. (color online) Mixed-dimensional vdWHs photodetectors: (a) structure of graphene/ZnO rod array heterostructure and (b) its sensing performance for UV light. (c) Schematic of graphene/ZnO nanowire heterostructure photodetector and (d) its sensing mechanism.

Distinct from the photovoltage device, a photogating photodetector is more like a field effect transistor and the detectable electrical signal results from varying conductivity in the device channel. Zhang *et al.* reported a graphene/ZnO nanowire photodetector working by photogating that achieved 1.8×10^5 A/W responsivity to UV light. The authors ascribed this outstanding performance to the efficient gain process in their device. As depicted in Fig. 5(d), electron–hole pairs are generated under illumination. Holes migrate to the ZnO surface and neutralize with the adsorbent O_2^- to release O_2, while electrons inject into graphene due to its higher concentration in the ZnO nanowire. The movement speed of electrons in graphene is ultrahigh, while the oxygen desorption process is slow. In this situation, one electron will re-circle many times in the graphene channel before it recombines with a hole, resulting in gain exceeding 10^6. Lee's group also constructed a graphene/ZnO heterostructure for photogating model detection.[54] They directly grew a ZnO nanorod array on graphene by using ZnO nanoparticles as growth seeds. The detection mechanism is similar to Zhang's device and 3×10^5 A/W responsivity was achieved in their device.[55]

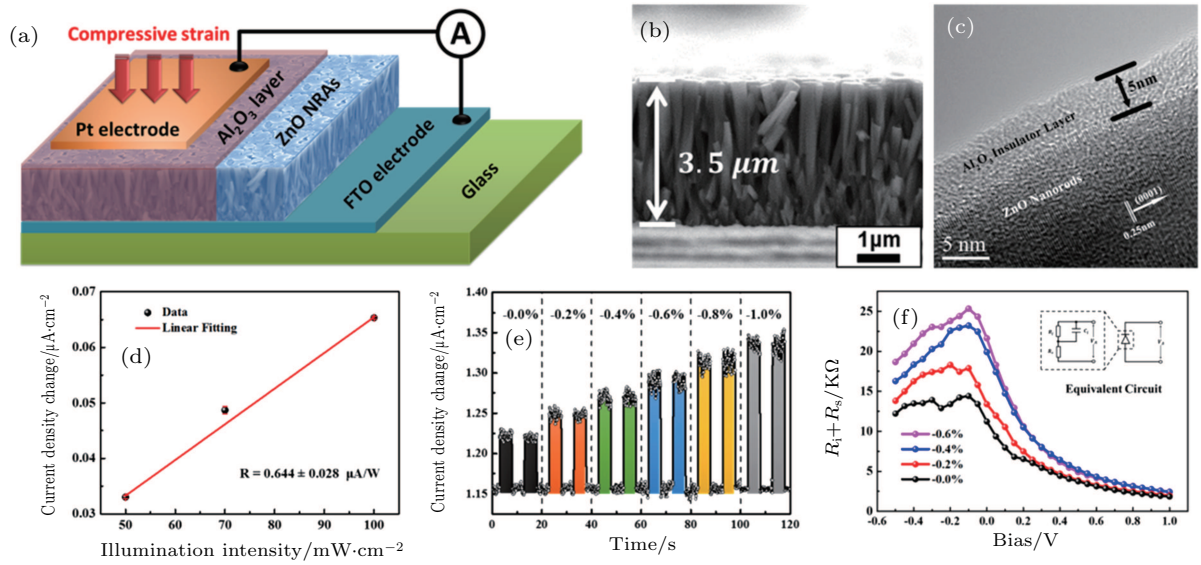


Fig. 6. (color online) Metal–insulator–semiconductor structured self-powered photodetector and its performance optimization under strains. (a) Schematic diagram of detector. (b) Side-view morphology of the ZnO nanorods array. (c) Morphology of the insulator layer. (d) Photoresponsivity of detector. (e) Photocurrent response under different compressive strains. (f) Resistance variation under different compressive strains. Inset is the equivalent circuit.

3. Strain engineering of photodetectors for performance optimization

It is well known that the working principle of most optoelectronic devices relies on the charge carrier separation/combination process at the interface rather than in the bulk.[56] Therefore, arbitrary regulation of interfacial electronic charged states could be implemented to modulate the performance or endow the device with novel functionality.[57–59] So far, multiple approaches have been introduced to precisely tailor of interfacial energetics, but most of them are restricted by complicated fabrication processes and narrowly restricted device configurations.[60,61] Due to their lack of inversion symmetry, semiconductor materials with wurtzite structure such as ZnO, GaN, and CdS could generate non-mobile piezoelectric polarization charges at the interface in the presence of mechanical deformation.[62] These interfacial ionic charges could tune energy band bending locally, thus exerting considerable influence on carrier transport characteristics and enabling improved device performance.[63,64]

For photodetectors with Schottky contacts, the Schottky barrier height (SBH) is significant for the detection sensitivity of the photon detector. By tuning the SBH through introducing local piezoelectric polarization charges, Wang's group demonstrated the piezoelectric effect on the responsivity of a metal–semiconductor-metal (M–S–M) structure ZnO micro/nanowire photodetector.[65] The results indicate that the sensitivity of the photodetector is respectively enhanced by 530%, 190%, 9%, and 15% upon 4.1 pW, 120.0 pW, 4.1 nW, and 180.4 nW UV light illumination onto the wire by applying a −0.36% compressive strain. It also indicates that the modulation ability of strain is much larger for weak light detection than for strong light detection. Basically, the photocurrent is generated at the interface of the semiconductor in a Schottky junction structure under illumination. To avoid the interference of tunneling current in the investigation of the piezotronic effect for performance enhancement in self-powered photodetector, a thin insulator layer of Al_2O_3 was deposited between the interface of the Pt and the ZnO nanowire array forming a metal–insulator–semiconductor junction as shown in Fig. 7. The ZnO nanorods synthesized by a hydrothermal method were well aligned on the substrate. And the insulator layer of Al_2O_3 was deposited uniformly on the surface of ZnO with a thickness of ~ 5 nm. The responsivity of the self-powered photodetector was about 0.644 μA/W under UV illumination without external power. Under compressive strain of 1.0%, responsivity increased to 1.78 μA/W. Based on the Schottky junction theory, this work was first demonstrate optimization of piezotronic effect in self-powered photodetectors by analyzing the resistance of the junction under different strains. The piezotronic effect has the strongest influence at the interface and gradually decays towards the quasi-neutral region of the junction.[66]

Visible and ultraviolet photo-detection with ZnO–CdS core-shell micro/nanowire was reported by Zhang and enhanced sensitivity involving piezopotential was also investigated.[67] Performance was improved more than 10 times when the device was subjected to a −0.31% compressive strain. The strain-induced piezopotential at the vicinity of the ZnO–CdS heterojunction facilitated electron injection from the conduction band (CB) of photoexcited CdS in the CB of ZnO, obtaining increased photocurrent and responsivity. A branched ZnO–CdS double-shell NW array on the surface of carbon fiber was synthesized via a solution-processed method and utilized as a visible/UV detector.[68] This novel

structure endows the device with much higher responsivity than that of devices based on ZnSe nanobelts or single ZnO–CdS core-shell NWs. Moreover, by applying −0.38% compressive strain, the performance of the photodetector was further enhanced by 69%. This is due to the positive piezoelectric charges generated in ZnO, which decrease the barrier height at the ZnO–CdS interface. The decrease facilitates transport of photo-generated electrons from ZnO and suppresses the trapping of photo-generated holes from excited CdS, enhancing device performance.

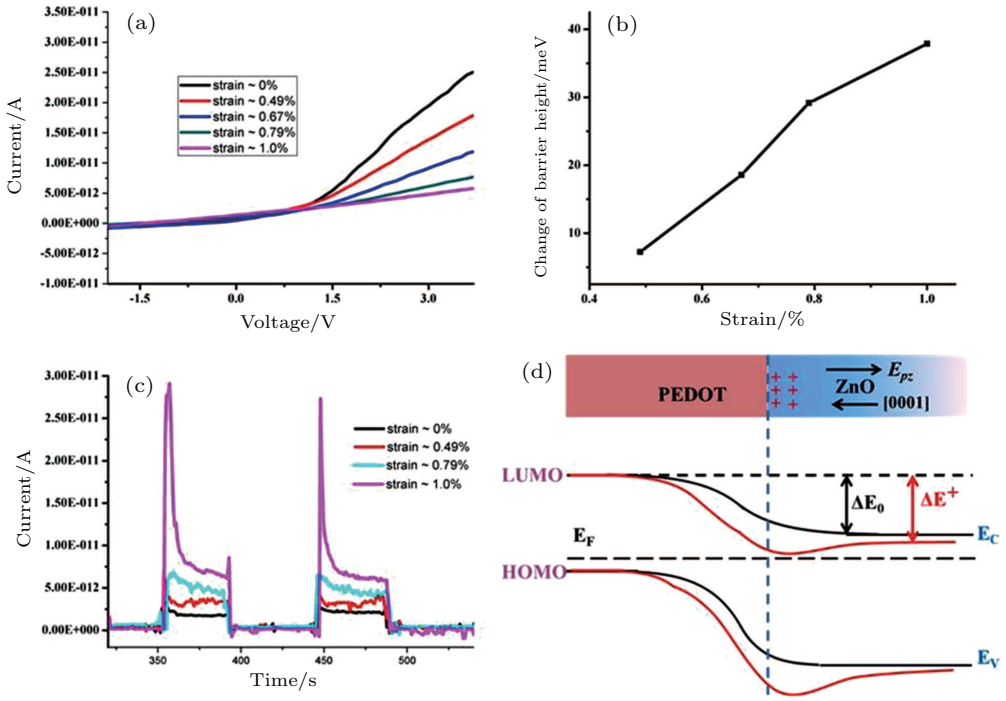


Fig. 7. (color online) (a) Typical *I–V* characteristics of the device under different strains. (b) Calculated barrier height change of PEDOT:PSS/ZnO heterojunction as a function of strain. (c) Time-resolved characteristic of UV response with different strains. (d) Schematic of energy band structure of PEDOT:PSS/ZnO heterojunction with and without the presence of strain, shown in red and black curves, respectively.

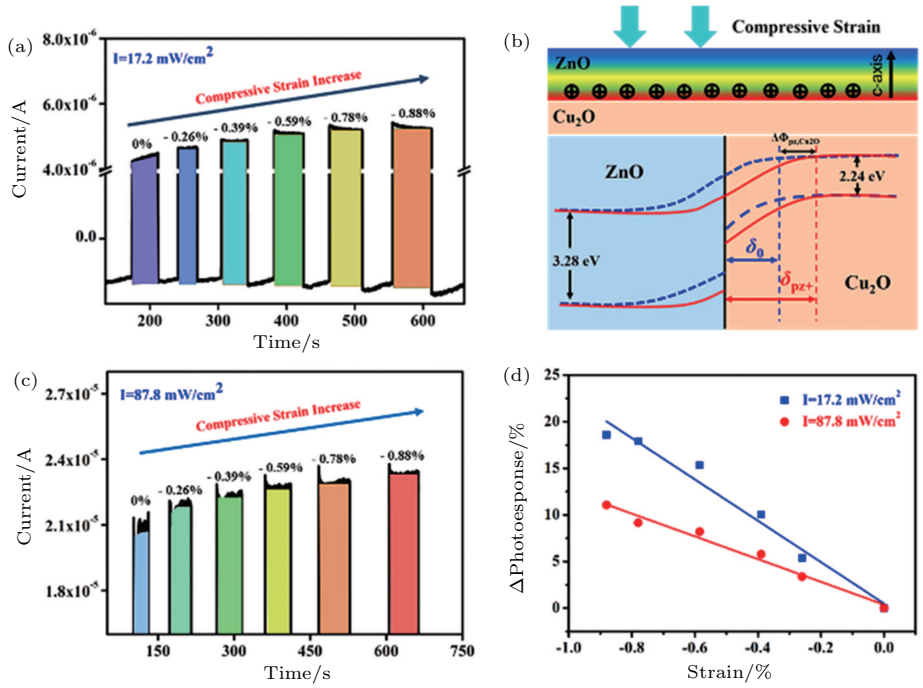


Fig. 8. (color online) Time-resolved photoresponse under different compressive strains with illumination density of 17.2 mW/cm^2 (a) and 87.8 mW/cm^2 (c). (b) Band diagram of Cu_2O/ZnO interface with and without positive piezopotential. (d) Calculated photoresponse enhancement vs. compressive strain.

The operation of a self-powered photodetector is based on separation of photon-generated electron–hole pairs within the built-in electric field at a p–n junction or a Schottky contact interface. So performance is exquisitely sensitive to the barrier height and strength of the internal field. One example has been verified based on a PEDOT: PSS/ZnO heterostructure, where the photocurrent at zero-voltage bias was significantly improved with increasing strain.[69] As depicted in Fig. 8(b), the increment of calculated barrier height is about 40 meV when applying a 1% tensile strain. This enhanced barrier height could produce a sharper built-in field at the interface and weaken the recombination of photogenerated electron–hole pairs. In this case, responsivity increased with the increase of applied strain, as shown in Fig. 7(c).

Piezoelectric polarization charges are capable of inducing remarkable modulation of the band shifting not only in ZnO but also in an adjacent semiconductor with which it forms a heterojunction.[62] Recently, we quantitatively demonstrated this in the Cu_2O/ZnO heterostructure.[70] As described in Fig. 7, under the illumination density of 17.2 mW/cm^2 provided by a solar simulator, photoresponse increases gradually with the increase of compressive strain and a 2.2% increment per 0.1% strain could be obtained. Due to the preferred $+c$ orientation growth of ZnO NRs, a permanent positive piezopotential would be generated at the Cu_2O/ZnO interface.[71] Like externally applied positive bias, this positive piezopotential can augment the depletion region in Cu_2O, as calculated in Fig. 8. The enlarged space charge region means that more excitons are generated and can be separated more effectively, enhancing photoresponse current. The modulation effect of piezopotential decreases with increasing illumination density, as shown in Fig. 8(c). Only a 1.2% increment of photocurrent per 0.1% was observed under illumination of 87.8 mW/cm^2. This is because more generated free charge carriers partially screen the piezopotential weakening the modulation ability.[72] Taking advantage of ZnO coupled semiconducting and piezoelectric properties is a promising and convenient way to boost the performance of optoelectronic devices, and this mechanism could be extended to other wurtzite materials.

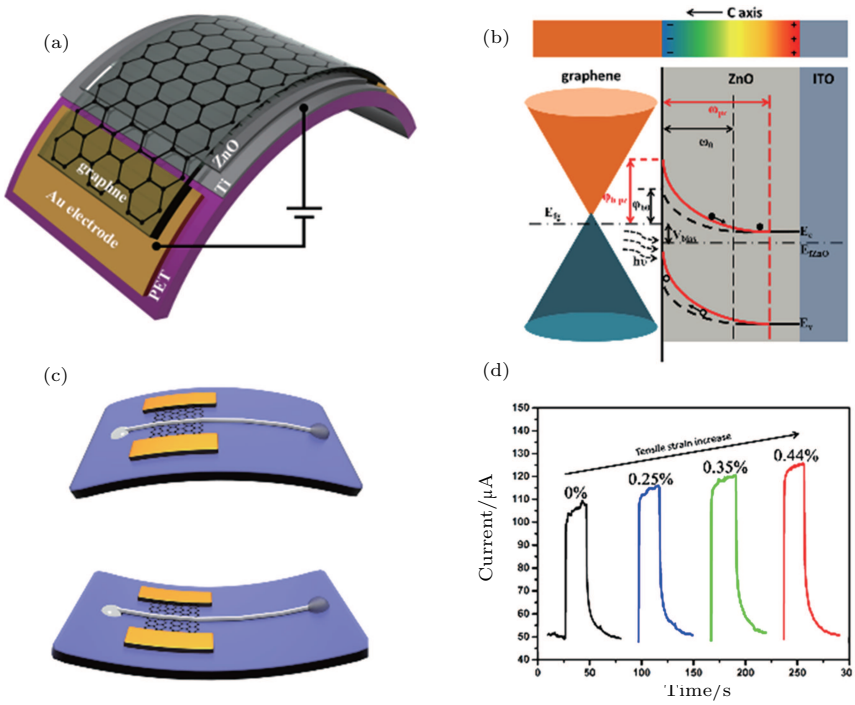


Fig. 9. (color online) (a) Flexible graphene/ZnO nanorod film heterostructure photodetector. (b) Strain induced band structure modulation in the device interface and its effect on the photocarrier separation process. (c) Flexible graphene/ZnO nanowire heterostructure and (d) its strain enhanced photosensing performance.

Strain modulation has also been conducted to boost the performance of mixed-dimensional vdWH photodetectors. Considering the absence of chemical bonds in the vdWHs, strain induced bond fracture or atomic reconstruction can be ignored, which degrades the electrical properties in traditional junctions. In addressing this concern, vdWHs could be an ideal platform to investigate strain modulated electronic or optoelectronic properties. Utilizing strain-induced interface band structure modulation, Zhang's group demonstrated that the performance of a graphene/ZnO nanorod film heterostructure can be enhanced by 18% under −0.349% compressive strain.[73] As illustrated in Fig. 9, the negative piezopotential leads to a rise of the Schottky barrier and enlargement of the depletion zone, both beneficial for photocarrier separation. Strain effect on mixed-dimensional vdWH photodetector which worked by the photogating mechanism was also

reported. It was found that positive piezopotential can be used to lower the Schottky barrier of a graphene/ZnO nanowire heterostructure. In this situation, electron injection from the ZnO wire to the graphene was significantly improved, dramatically enhancing the device responsivity.

4. Conclusion and prospects

In this review, recent advances in 1D ZnO-based optoelectronic devices and solar photovoltaics have been presented. Some effective approaches to improving device performance have been described, such as optimizing material and device geometry, semiconductor band-structure engineering with piezoelectric polarization, and interface modulation. They not only impact micro/nanosystems for energy harvesting technologies but also inspire invention of new electronic devices based on 1D ZnO nanostructures. More research should be inspired to address the challenges inhibiting practical applications of 1D ZnO-based optoelectronic devices. First of all, one of the major constraints on device performance is excessive shunting due to poor contacts or impurities at the junctions. In this regard, improving crystallinity and controlling defects in 1D ZnO nanostructures should be considered. Besides, novel design of devices (e.g. proper surface treatments, regular nanopatterning, mixed dimensional Van der Waals heterostructures, etc.) can offer alternative methods to improve device performance to meet the demands of the next generation of electronics and optoelectronics.

With the feature size of nanodevices approaching atomic scale, the materials are sensitive to external physical field and the chemical environment based on lots of experimental evidence. Thus, it is essential to find out the fundamental optimization pattern of optoelectronics under multi-field coupling effects (such as strain, thermal, illumination, magnetic field).

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