Review on ZnO-based piezotronics and piezoelectric nanogenerators: aspects of piezopotential and screening effect

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Abstract
Among various piezoelectric materials, ZnO has attracted a great deal of attention due to facile preparations and exceptional semiconductor characteristics compared to other conventional piezoceramics or organic piezoelectric materials. One of the issues hindering ZnO from progressing into applications is the screening effect, where the intrinsic piezopotential generated upon mechanical deformations is screened and becomes waned or even diminished by the presence of intrinsic free carriers in ZnO. Consequently, ZnO-based piezoelectric devices often suffer from low output voltages, resulting in low total output power generation even though the output current could be larger than those made of insulating piezoelectric materials, such as PZT, polyvinylidene fluoride, and barium titanate. It is therefore vital to fully understand the impact of the screening effect and produce strategies to handle this issue in the context of piezotronics and piezoelectric nanogenerators (PENG). Therefore, this article presents a comprehensive review of growth methodologies for various ZnO nanostructures, structure modifications, effects of free carriers on the screening effect and strategies for device applications, including strain-gated transistors, PENG and piezotronic sensors for gas, humidity and bio-molecules etc.

1. Introduction
Piezoelectric effects exist in both natural, including quartz, Rochelle salt, and topaz, and man-made piezoelectric materials, such as barium titanate (BaTiO3) and lead zirconate titanate (Pb(ZrxTi1−x)O3) (referred to as PZT) etc. Due to the growing environmental concerns of toxicity in lead-containing devices and demanding for developing multifunctional devices, there has been a push to develop lead-free piezoelectric semiconductor materials, such as wurtzite families of zinc oxide (ZnO) [1, 2], gallium nitride (GaN) [3, 4] and indium nitride (InN) [5, 6], etc. They provide not only reasonably good piezoelectric properties for energy harvesting devices but optoelectronic properties for various piezotronic devices. Of them, ZnO has emerged as the most popular for the following reasons: (a) various high quality and uniaxially oriented variants of ZnO nanostructures with multi-dimensions, including nanowires (NWs), nanorods (NRs), nanosheets (NSs), nanodiscs and thin films etc; (b) economic growth on crystalline or amorphous as well as hard or flexible substrates and compatible with technologically vital materials, like silicon or polymers; (c) biologically compatible and environmentally friendly materials; (d) easy to tune optoelectronic properties by doping. Of note, one dimensional (1D) and two-dimensional (2D) ZnO nanomaterials are ideal for piezotronics and piezoelectric nanogenerators (PENG) because geometry and size favor tuning of Schottky barrier height (SBH) and higher piezopotential generation through higher piezoelectric coefficient and larger elastic deformation upon only applying tiny physical stimulus. Moreover, the large surface area is beneficial for surface functionalization to advance physical and chemical properties.

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Piezoelectric effect in ZnO

Piezoelectric effect is related to the generation of an electric dipole in response to external stress and was first observed in quartz crystal by Jacques and Pierre Curie in 1880 [7]. They also validated the inverse piezoelectric effect where the crystal deformed in response to application of electric field. The piezoelectric effect in wurtzite materials resorts to the non-centrosymmetric structure. In this regard, ZnO is a model material with tetrahedrally coordinated Zn$^{2+}$ cations and O$^{2-}$ anions within the lattices as shown in figure 1. Application of mechanical stress along the c-axis of ZnO causes the displacement of the centers of the positive and negative charges, resulting in dipole moments. The superposition of all these dipole moments across the crystal produces a substantial potential difference along the polarization direction, known as piezopotential [8]. This piezopotential can be used to control the electric current flowing through external circuit for electricity output or carrier transportation in piezoelectric semiconductors as the virtual gate terminal.

3. ZnO-based piezoelectric devices

Based on the working mechanism and applications, piezoelectric devices can mainly be categorized into piezoelectric-gated field-effect transistor (PG-FET) and PENG.

3.1. Piezoelectric-gated field-effect transistor

Figure 2(a) shows how a typical conventional NW-based FET works with three terminals, including gate, source and drain. The voltage applied over the gate terminal can modulate the current from the source to the drain electrode by trapping and depleting the carriers in the NW. However, the gate electrode is now replaced by piezopotential in the PG-FET as shown in figure 2(b), where deflecting the NW modulates the piezopotential. Thus, the electric current through the two electrodes is controlled by the degree of bending for modulating the piezopotential as the gate (figures 2(b)–(d)) [9–13]. The mechanism responsible for the conductance change in figure 2(d) is shown in figure 2(e)–(f). A piezo potential across the NW was built by the deformation, one side positive and the other side negative (figure 2(e)). The available free carriers in the n-type ZnO NW will be attracted and get trapped at the positive piezopotential side (figure 2(f)), leaving behind a depletion region at the negative piezopotential side (figure 2(g)). Thus, effective carrier density is reduced. It is noteworthy here that the charges produced by the piezoelectric effect during deformation are rigid, ionic and affixed to the atoms and cannot be depleted by free charges. Therefore, the positive potential side is screened by free carriers. Consequently, the conduction channel width decreases with the increase of the NW bending, while the depletion region increases, resulting in current decrease.

However, in the case of piezotronic devices made of either p–n or Schottky junctions with one of the materials being piezoelectric semiconductor, the built-in barrier height at the interface can be modulated by external stress and controls the current, on which modern electronic devices and sensors are based. For example, if a c-axis oriented n-type piezoelectric ZnO forms junctions with non-piezoelectric p-type semiconductor or metal, positive charges are created at the interface in the ZnO side upon compression along the c-axis, modulating the barrier height. The working principle of both piezotronic p–n (piezoelectric) and piezotronic Schottky diodes and the corresponding IV curves are depicted in figure 3.

In case of either p–n junction or Schottky contact, built-in potential or SBH is developed at the interfaces in equilibrium as shown in figure 3. After applying an external force to the piezoelectric semiconductor, a positive/negative piezopotential is generated due to tensile/compressive strain at the semiconductor interface side and effectively modify the built-in potential or SBH, resulting in control of charge transport via piezopotential across the interface. Thus, the piezoelectric crystal orientation as well as the type and
Figure 2. (a) Schematic of a conventional FET. (b) The principle of the PE-FET. (c) SEM images, showing the five typical consecutive bending cases of a ZnO NW. (d) Corresponding \( I-V \) characteristics of the ZnO NW. (e) Simulation of the strain distribution along the bent ZnO NW. (f) The carrier trapping effect and (g) the creation of a charge depletion zone. Reprinted with permission from [10]. Copyright (2006) American Chemical Society.

Figure 3. (a)–(d) P-piezoelectric n junction (e)–(h) and metal–piezoelectric semiconductor Schottky contacts for the distribution of (a), (e) piezoelectric and space charges at \( V = 0 \). (b), (f) built-in electric field, (c) potential distribution, and (d), (g) energy band diagram where the solid and dashed lines in all the figures represent whether the induced piezopotential is or not considered, respectively. (h) Current–voltage curves at strains ranging from \(-1\%\) to \(1\%\) for p–n junction device. [14] John Wiley & Sons. [Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim].

The magnitude of external strain can tune the local contact characteristics. This concept was firstly introduced by Wang et al over a decade ago [1, 8, 10, 11].

3.2. ZnO-based nanogenerator
ZnO-based PENGs convert mechanical energy into electrical energy. A generalized device structure in figure 4 demonstrates the underlying mechanism. The piezopotential generated inside ZnO upon compression is the driving force of the current flow, hence electricity output, through external circuit toward balancing the potential difference at the two contacts. If the induced piezopotential overcomes the built-in SBH at the Schottky contact while the other junction is Ohmic contact, the current will flow through ZnO in one direction working as a DC nanogenerator. However, if the SBH is too high to overcome, current flow through the external circuit is blocked by the Schottky contact and drifts back when the piezopotential is diminished upon the removal of the applied forces working as an AC nanogenerator. Thus, the output form of PENGs is dependent on the \textit{in situ} rectifying behaviour of the Schottky contact [16]. In order to obtain AC PENGs with high output, the metal electrode forming Schottky contact is often replaced with insulating polymer poly(methyl methacrylate) to produce better charge accumulation potential barrier [17, 18].
AC PENGs can be perceived as capacitive configuration, where the strained ZnO NWs act as a dielectric material with polarized dipole moments.

4. Piezopotential screening effect in ZnO

ZnO is intrinsically n-type semiconducting materials with hexagonal wurtzite structure and the carrier type and concentration can be changed via doping of different species. The remaining free charge carriers in ZnO will interact with piezopotential through piezoelectric field, causing the redistribution of the carriers in the piezoelectric material. On a bent ZnO NW, positive and negative piezo-charges and piezopotential are created at the stretched and compressed side, respectively, where the induced piezo-charges are non-moveable under external electric field. Under these circumstances, the free electrons that reside in the conduction band of n-ZnO are attracted towards the positive side and partially weaken the piezopotential, known as the screening effect. The negative piezoelectric potential side is unaffected under the low donor concentrations [19]. Theoretical and experimental attempts have been paid to understand the screening effect in ZnO playing the pivotal role in the context of PENGs and piezotronics.

4.1. Theoretical verification of the screening effect

It is noteworthy here that the Lippman theory is often adopted to describe bent piezoelectric NWs of extremely low carrier concentrations and thus conductivity is neglected. Evidently, this theory cannot be directly applied to semiconductors, especially with higher carrier concentrations. In 2009, Gao et al presented a macroscopic-statistical model to study the screening effect of the c-axis oriented ZnO NWs with moderate conductivity theoretically in figure 5 [19], where the piezopotential was calculated based on finite element analysis by solving the differential equations dealing with the distribution of free carriers.

The calculations were performed for a ZnO NW (a = 25 nm and l = 600 nm) with \( N_D = 1 \times 10^{17} \) cm\(^{-3}\) under the external force of \( f_y = 80 \) nN at \( T = 300 \) K and the piezoelectric potential (\( \varphi \)) distribution is presented for the cross-section plane at \( x = 0 \) and \( z = 400 \) nm with the corresponding equal-potential lines in figures 5(a) and (b), respectively. For comparison, they also performed the same calculations for an insulating ZnO without any free carriers but at the unrealistic temperature of 300 000 K in figures 5(c) and (d). By comparing these two cases, while the negative potential is well preserved, the screening effect is pronounced at the positive potential side where \( \varphi \) is greatly reduced from ~0.3 V for the insulating ZnO (figure 5(d)) to less than 0.05 V (figure 5(b)) for the moderately doped ZnO. The reduction in positive potential, referred to the screening effect, arises from the in-flow of free electrons, accompanied by the formation of an electron depletion region in the negative potential side.
4.2. Experimental verification of screening effect

To understand the screening effect by experimental approaches, endeavours have been attempted either by growing ZnO nanostructures with various doping concentrations or forming different device structures. Yang et al realized the screening effect in highly dense NR arrays through tunnelling, which can be greatly reduced by patterned growth of ZnO NRs to prevent electrons from tunnelling, leading to the output current enhancement of up to 6 times [20].

Recently, Tian et al studied again the suppression of screening effect on discretely patterned ZnO NRs array in 2020 by piezo-response force microscopy (PFM) to reveal the electron dynamics [21]. The patterned ZnO NRs array as shown in figure 6(a) were grown by hydrothermal method and patterned by lithography. The PFM setup with the area scanned over different regions (i to v) of the patterned ZnO NRs are also schematically shown in figure 6(a). The schematics in figure 6(b) demonstrate the different degree of electron tunnelling from neighbouring NRs acting on the NR located either in the center or edge of one discrete pattern under normal force by the probe to generate a positive and negative piezopotential on both ends. In this scenario, the NR in the periphery of the pattern is expected to generate a larger piezopotential due to less screening effect as compared to the one in the middle area, which is confirmed by PFM amplitude profiles in figures 6(c) and (d). The results reveal the potential screening effect generation mechanism in NR arrays through tunnelling and offer a design concept to further improve the piezoelectricity for ZnO NRs.

In 2015, Lu et al investigated systematically the piezo-phototronics effect dependence on the carrier concentrations of a Schottky diode based on ZnO NRs under UV illuminations [22]. The diode becomes more conductive with increasing power density of the illuminations presented in the I–V curves in...
Figure 6. Direct detection and characterization of potential screening effect. (a) Schematic of the PFM and the adoptive testing approach. (b) Schematic of the phenomenon of screening effect in different NR region. (c) The piezo-response amplitude 3D images of different areas in the patterned ZnO NRs. (d) Overlay of the extracted amplitude line profiles from different areas in (c). Reprinted with permission from [21]. Copyright (2020) American Chemical Society.

Figure 7(a) due to increased photoexcited free carrier concentrations in the ZnO NRs. With the capability in altering the carrier concentration by UV illuminations, the piezo-phototronics effects are examined in figures 7(b)–(e) under different illumination conditions. They observed a steady reduction in current with compression for all the illumination power densities, attributed to the enhanced SBH of ZnO/Au from the induced negative piezopotential. More significantly, the dependence on strain becomes less sensitive with increasing UV illumination power and even reaching constant current with strain under the highest power of 1.2 mW cm⁻² illumination, where the piezopotential vanishes by the screening effect from the photoexcited carriers. The piezo-phototronics effect is best represented by the SBH change with strain in figure 7(f), where the variation of the SBH change with illumination power elaborates the effect of carrier concentration on screening effect. The results show that piezopotential can be completely eliminated by the screening effect. Furthermore, Hu et al [23] explored the screening effect of ZnO NWs in the temperature ranging from 77 K to 300 K and suggested that lowering the temperature results in a largely enhanced piezotronic effect. Similar phenomena of temperature dependent screening effect were also observed in other semiconducting materials [24, 25]. Pan et al presented the effect of carrier concentration on piezotronics and piezo-phototronic effects in ZnO thin film transistors and paved a path to enhance/optimize the performances of electronic/optoelectronic devices [26].

5. ZnO-based piezotronics and nanogenerators for applications

By correlating the mechanical stimulus from the environmental factors of interest to output signal, various piezotronic devices have been realized with the application in power generation, water splitting and sensing for biomolecules, humidity, pressure/strain, photons, and gas etc. The performance of all the devices essentially revolves around the manipulation of piezo potential and needs to be devised.

5.1. ZnO-based piezotronic strain/pressure sensor

Strain sensors based on NWs, nanotubes (NTs) or thin films have been extensively developed for possible use in portable and wearable devices. However, the materials integrating piezoelectric and semiconducting
properties are most suitable strain sensors where strain can dramatically tune the current flow by the change of SBH [14, 27–30]. In this regard, ZnO have received significant attention for the fabrication of strain/pressure sensors due to high crystal quality, different morphology available, high gauge factor [12].

The first ZnO-based piezotronic strain sensor was introduced by Z. L. Wang et al. in 2008 [12]. The strain sensor was made by bonding a ZnO piezoelectric flexible NWs laterally on a flexible PS substrate and subsequently encapsulated in a PDMS thin film as shown in figures 8(a)–(b). They demonstrated the excellent stability, fast response of strain sensors with high gauge factor of up to 1250. The force dependent IV curves reveals that the device is controlled by the change of SBH and the relationship between strain and SBH is linear in figures 8(c) and (d).

The change of SBH, the factor for strain sensor sensitivity, can be deteriorated by the screening effect, which can be mitigated by forming local depletion regions through Schottky contacts. Therefore in 2016, Li et al decorated ZnO NWs with Au nanoparticles (NPs) to form local Schottky contacts, depleting free carrier concentrations in ZnO NWs and thus reduced the screening effect [31]. The Schottky barrier either forms
Figure 9. (a) Schematic of Au NPs decorated ZnO based device with free and external load conditions, showing a change in depletion width. I–V curves of strain-gated transistor at different strain conditions (b) without Au NPs, and with Au NPs (c) under tensile strain and (d) under compressive strain. Reprinted from [32], Copyright (2016), with permission from Elsevier.

over metal/ZnO interface on top or Au NPs/ZnO NWs interface at sides acting as gate to modulate the depletion width and thus the current flow through the ZnO NW upon external stressing (figure 9(a)) [31, 32]. Figures 9(b)–(d) reveal that the current change in the strain-dependent IV curves of the ZnO NW with Au NPs is much higher than that without Au NPs, supporting the enhancement of strain sensitivity by suppressing the screening effects with Au NPs decoration.

Piezotronic ZnO-based strain sensors can be further improved if made flexible devices by modifying the active matrix using combination of materials and forming composite materials. In this regard, Gullapalli et al. in 2010, demonstrated a strain sensor made of low temperature synthesis of a nanocomposite material containing ZnO nanostructures embedded in a paper (cellulose) matrix coated with a very thin gold layer as an electrode, achieving the sensitivity of up to around 0.01% of strain [33]. In the same directin, Xiao et al. in 2011 introduced a stretchable strain sensor by incorporating ZnO NW/polystyrene nanofiber hybrid structure on PDMS film, which can be strained up to ≈50% with the gauge factor of ≈116 [34]. They have also demonstrated to apply this strain sensor for identifying the finger motion by the corresponding output current. However, in 2014, Zhang et al. explored a vertically-aligned ZnO NW/PDMS based strain sensor to improve the performance and sensitivity of sensors with the gauge factor of 1813 at 0.8% of strain [35].

Besides the several above-mentioned methodologies for the enhancement of sensitivity of pressure sensors, porosity in thin film and nanomaterials has also emerged as one of the novel strategies. In 2019, Su et al. [36] have developed porous ZnO NWs by annealing hydrothermally grown NWs under H2 environment in order to enhance the sensitivity of force sensors. The sensitivity expressed both by the current drop percentage and the change of SBH, of the device have significantly improved by the porosity in figure 10, where the pore-enhanced working mechanism was also justified by theoretical simulations. In this way, they observed 6 fold enhancement in force sensitivity upon incorporation of pores in NWs.

The pore mechanism has attempted on ZnO thin films very recently in 2021 for practical applications by Lee et al. [37]. The porous ZnO thin film was developed by annealing sputter ZnO thin film on Si at elevated temperatures. The force-dependent I–V curves for the pristine and porous ZnO thin films grown at 850 °C as shown in figures 11(a) and (b) clearly demonstrate the higher degree of decrement of current for the porous film as compared to the pristine film. The higher sensitivity of the porous ZnO thin film pressure sensor is represented by the SBH change in figure 11. They have reported the around 7 fold enhancement in SBH after incorporation of pores in thin film via annealing.

5.2. ZnO-based piezotronic bio-sensors
Electrical stimulation of cells and tissues has been traditionally exploited in the clinical practice for a wide range of pathological conditions. Biosensors for identifying biomolecules have excellent uses in medical diagnostics, food/nutrition industry and environmental examination. In this regard, ZnO of different
morphologies has been intensively probed for biosensing due to low cost and biological friendliness, where the biomolecules adsorbed on the surface can act as a gate to modulate the electrical properties. The coupling of biosensing and piezotronic properties of ZnO into a single process may realize a new self-powered biosensor where the output of the device is modulated by the adsorption of biomolecules. The possibility to sense an indirect electrical stimulation, by means of piezoelectric materials, is therefore of outstanding interest for all the biomedical research, which emerged in the latest decade as a most promising tool in many bioapplications [38, 39]. Thus, a ZnO-based piezotronic biosensor involves with the adsorption of the target biomolecules at the functionalized surface and the change in output signal of the device in response to potential physico-chemical reactions of the biomolecules via pH, temperature and chemical composition [40]. In 2014, Zhao et al explored self-powdered bio-sensors by growing ZnO NW arrays on a conducting Ti foil with Au electrode to detect biomolecules Immunoglobulin G (IgG) of different concentrations as shown in figure 12 [41]. The surface of ZnO NWs was modified with gold nano-particle–anti-IgG (AuNP–anti-IgG) conjugates in order to enhance the proficiency of immobilizing the IgG antibodies. They observed the linear decrease in output voltage in response to increasing IgG concentration. The positively charged IgG acts as a positive potential gate, causing the increase of the electron density in the ZnO NWs. Thus, the screening effect is enhanced, leading to the piezoelectric output reduced.

In 2014, Neveling et al explored the self-powered PENG based on Au/ZnO NWs/Au double Schottky diodes as biosensors for the detection of IgG as shown figure 13 [42]. Lysosome was employed as an antigen, covalently immobilized onto Au-coated ZnO NWs by using self-assembled monolayers. Linear dependence of the output voltage was reported on the concentration of antibodies in the range 50 ng ml\(^{-1}\) to 1 µg ml\(^{-1}\) and turns to non-linear dependence beyond that as in figures 13(b) and (c). In the same year, Zhao et al proposed a similar ZnO NW-based device but incorporated the SiO\(_2\) as gate insulating to improve the structural and electrical stability of device [43]. In this way, the detection limit of IgG was up to 5.7 ng ml\(^{-1}\).

Cytochromes P450 (CYPs) plays a vital role in metabolism of drug and chemicals. Being a member of the CYP family, cytochrome P450 2C9 (CYP2C9) is engaged in the oxidation of roughly 16% of therapeutically
Figure 12. Piezoelectric output of the ZnO-based biosensor device after being immersed in different concentrations of IgG solution. (a) None IgG, (b) $10^{-7}$ g ml$^{-1}$, (c) $10^{-6}$ g ml$^{-1}$, (d) $10^{-5}$ g ml$^{-1}$, (e) $10^{-4}$ g ml$^{-1}$, (f) $10^{-3}$ g ml$^{-1}$, (g) relationship between the piezoelectric output of the device and the concentration of IgG, and (h) dependence of the response on the concentration of IgG. Reprinted from [41], Copyright (2014), with permission from Elsevier.

Figure 13. Schematic of the nanoforce ZnO NW array-based bio sensor. Biosensor sensitivity curve (b) of voltage output against antibody concentration (10 ng ml$^{-1}$–20 µg/ml), and (c) linear curve extracted for the concentration from 50 ng ml$^{-1}$ to 1 µg ml$^{-1}$. Reprinted from [42], Copyright (2014), with permission from Elsevier.
critical drugs. Therefore, it is essential to examine drug metabolism reactions employing CYPs to detect the related problems such as in the field of drug development. In 2015, Wang et al developed a single ZnO NW sensor decorated with CYP2C9/CPR-microsomes and successfully detected the drug of tobutamide (0 µM to 4 µM) as linear output current under compressive forces via piezotronic effect \[44\]. A similar type of device was developed by Cao et al in 2016 for the detection of human immunodeficiency virus 1 gene, where a single ZnO NW with Schottky contacts was modified by single-stranded DNA for label free negatively charged target DNA (c-DNA) detection \[45\]. They found that the resulting current density decreases with rising concentration of c-DNA, but augmented with increasing strain attributed to the negative charge of c-DNA and piezotronic effects.

In 2016, Xue et al fabricated an e-skin sensor to detect glucose level in blood by utilizing piezo-enzymatic-reaction of GOx@ZnO (GOx: glucose-oxidase) NW arrays \[46\]. The fabricated flexible e-skin can work in liquid medium and power itself via converting human movement to electrical energy, where the output voltage is reduced with increasing glucose concentration due to the screening effect induced by the surface carrier density from the enzymatically decomposed glucose molecules. In 2020, Lan et al, also synthesized a single ZnO NW based label free protein kinesis sensor, where piezotronic effect was applied to enhance the change in current due to protein concentration by applying external force as shown in figure 14 \[47\].

5.3. ZnO-based piezotronic Gas sensors
Our surrounding atmosphere contains several volatile/nonvolatile and toxic gases released by the industries, vehicles and detection of these gases is of paramount importance for a safe and healthy life. Although significant advancements have been made on gas sensors, the sensitivity, selectivity, response kinetics and reliability still need to be improved for real industrial applications. Of them, ZnO NW-based devices have excelled gas sensing performance and the sensitivity can be further enhanced by piezotronic effect \[48\]. The oxidizing or reducing gas adsorbed on the ZnO NWs surface have capability to modify the free-electron density as well as the screening of the piezoelectric polarization charges, thus affecting the piezoelectric output of ZnO.

Niu et al \[48\] fabricated oxygen sensor by using ZnO NWs (length = 100–300 µm, diameter = 800 nm) on flexible substrate and piezotronic effect is used to enhance the sensitivity by modulating the SBH. At the oxygen pressure of 16 torr, the current drop in the sensor is increased with the increase in the applied strain and the current drop is increased up to nearly 45% or 16.8% at the forward biased of 1 V or the reverse biased condition of $-1$ V, respectively. The asymmetry in the current between positive and negative bias is due to the piezotronic effect describing the regulation of SBH from positive/negative piezocharges. The SBH at both ends of the sensor follows an increasing trend with oxygen pressure at a fixed strain (0.2%) and opposite when the sensor is subjected to various strain (0%–0.2%) under a fixed oxygen pressure. Therefore, the piezopotential regulates the SBH effectively to enhance the sensitivity of the sensor.
Figure 15. Piezoelectric output voltage of the gas sensor at room temperature upon exposure to dry air (a), 400 ppm (b), 800 ppm (c), and 1200 ppm ethanol (d), respectively. The compressive strain applied to the device is 0.01%. The insets are the enlarge views of the piezoelectric output. (e) The dependence of the piezoelectric output voltage and the sensitivity on the concentration of ethanol gas. (f) The piezoelectric output current of the device at room temperature upon exposure to dry air, 400, 800, and 1200 ppm ethanol. Reprinted from [49], with the permission of AIP Publishing.

Furthermore, Xing et al have coupled the piezotron ice effect of ZnO NW arrays decorated with Au NPs for room-temperature self-powered active ethanol sensor using Au/ZnO NW arrays [49]. The piezoelectric output of Au/ZnO was used as power source as well as response signal to ethanol at room temperature in figures 15(a)–(d) where the output voltage reduced from 1.54 V (in air) to 0.43 V in exposure to 1200 ppm ethanol, attributed to oxidizing nature of ethanol donating electron to ZnO NWs and increasing screening effect. In the same concept, in 2013, Xue et al utilized the screening effect of ZnO NRs over Ti substrate with Al electrode as self-powered H2S gas sensors [50], and demonstrated that the detection limit of H2S can reach as low as 100 ppm.

5.4. ZnO-based piezotronic humidity sensors

Humidity affects almost everything around us including the electronic equipment, food, medicine and the detection/monitoring of this important parameter is of paramount importance. Recently, piezotronic effect [51, 52] is effectively used to tune the SBH by the application of strain thereby generating a piezopotential due to the polarization of piezocharges and enhance the humidity sensing properties in semiconductor NWs.

Hu et al [51] reported the humidity sensing performance of a ZnO micro/NW based on piezotronic effect where the sensing property is significantly enhanced under strain. Whereas under strain free conditions, the current decreases from 365.0 nA to 8.72 nA as increasing humidity from ~15.0% to ~66.0%, and the current decrease is significantly higher under 0.2% strain (884 nA to 12.9 nA) implying the enhanced sensing performance due to piezotronic effect. Under humid conditions, water molecules get adsorbed on the sensor surface forming hydroxyl ions, reducing the carrier concentration and electrical conductivity due to the formation of an electron depletion layer. In contrast to strain free conditions, the SBH decreases with compressive strain as the piezotronic effect, simultaneously enhancing the signal level, sensitivity and the sensing resolution of the Schottky contacted ZnO micro/NW humidity sensor. The optimized compressive strain of ~0.22% yield the best responsivity of 1240% investigated. Similar enhanced humidity sensing performance has also been reported for S-doped ZnO NW array sensors as shown in figure 16 [52]. Under the loading weight of 12.5 cm−2 at 50 °C operating temperature, the RH performance of the sensor promptly improved ~3 orders of magnitude at 80% RH.

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5.5. ZnO-based piezo-phototronic photo-sensor

The coupling among optical, mechanical, and electrical properties of the ZnO-metal interface through Schottky contact offers new paths for enhancement in photonics devices, called piezophototronic devices [29]. Wang et al in 2010 introduced first the effect of piezopotential on photocurrent under different strain and laser illumination [53]. They observed that piezo-potential generated upon applied strain can tune the effective SBH at Schottky interface of ZnO NWs/metal in response to light illuminations, consequently enhancing the output current of the photocell. In the same year, Yang et al also incorporated piezo-phototronic effect to enhance the responsivity of ZnO-NW-based photodetectors by 530%, 190%, 9%, and 15% upon light illumination of 4.1 pW, 120.0 pW, 4.1 nW, and 180.4 nW UV, respectively, under 0.36% compressive strain [54]. The tuning of SBH at the metal semiconductor interface contact is produced local piezopotential. A systematic explanation of the tuning of SBH with change of strain and illumination light intensity with corresponding band diagrams is given in figure 17. Figure 17(a) shows numerically calculated piezopotential upon deformation, modulating effective SBH and thus the change in photocurrent and responsivity of the device. Therefore, compressive strain decreases the SBH at the drain contacts and the photocurrent and responsivity will be enhanced in the dark as shown in figure 17(b). Nevertheless, increasing light intensity causes reduction in responsivity due to photo-excited carriers induced screening effect as shown in figure 17(c).

Moreover, further improvement has been attempted through microstructure and morphology of ZnO nanomaterials as well as device design for better operation of piezo-phototronics. For example, Wang et al have grown the Al-doped ZnO NWs laterally over flexible SiO$_2$-coated steel substrate [55]. They reported linear response of the photocurrent on tensile strain up to 5.6% at 1 V bias because SBH is reduced resulting from the piezo-photonic effect. Zhang et al [56] developed a single ZnO/CdS NW photodetector demonstrating superb responses on broad-scale visible/UV. Through piezophototronic effect, the performance of the ZnO/CdS photodetector was shown to be enhanced more than 10 fold at $-0.31\%$ compressive strain and under the illumination of visible and UV light.

Lu et al [57] suggested that the stronger built-in field can be induced via interfacial piezopotential, which boosts the separation and extraction of the photon at the interface of ZnO/Au Schottky junction. They observed linear increment in photocurrent under applied tensile strain and acquired 440% improvement in
Figure 17. Schematic energy band diagram illustration for tuning the SBH by piezopotential. (a) Simulation of the piezopotential distribution in the wire under compressive and tensile strain. SBH tuned by piezopotential under compressive strain (b) in the dark and (c) with light illumination. Reprinted with permission from [54]. Copyright (2010) American Chemical Society.

photocurrent and a 5 fold enhancement in sensitivity under a strain of 0.580%. In the same year, Zhang et al, performed a novel laser compatible in-situ transmission electron microscopy (TEM) technique to compare the photo-response of CdS nanobelt and CdS/ZnO heterostructure and obtained a notably higher on/off ratio and quicker response time for the heterostructure due to the higher surface trap states [58]. In 2016, Liu et al designed a graphene/ZnO NRs film hybridized photodiode in figure 18 and the device responsivity was enhanced from 71.64 to 84.94 A W⁻¹ at −0.349% compressive strain by increasing SBH at the interface with the wider depletion region, which in turn effectively modulates the carrier separation at the junction [59]. In 2018, Peng et al [60] designed a self-powered UV photodetector based on ZnO NRs with an iodine-free quasi solid-state electrolyte and demonstrated 63% enhancement in responsivity under the bending angle of 60°. The enhancement was ascribed to modification effect of electrolyte at interface of ZnO. Zeong et al [61] synthesized WZ ZnO/WZ ZnS and WZ ZnO/ ZB ZnS core/shell structure separately and explored TEM for extensive characterization as shown in figure 18. They demonstrated that WZ ZnO/WZ ZnS core/shell photodetector yielded higher output current and photoresponsivity as compared to WZ ZnO/ ZB ZnS counterparts.

While most of the research have been focused on the non-ferroelectric piezoelectric ZnO, Dai et al in 2019 introduced a photodetector made of 2D vanadium-doped ZnO ferroelectric semiconductor NSs over p-Si substrate as a p–n type heterojunction [62]. Incorporation of ferroelectricity with piezophototronics leads to the improvement in current rectification and the photoresponsivity up to 2.4 fold at +1 V under compressive strain as compared to non-ferroelectric ZnO counterparts. This V doping induced dipoles have ability to alter the local band profile near the p–n junction, which stimulates greatly the generation, separation, and transportation of photocarriers for the enhancement. In order to approach for practical application of piezotronic photosensors, Chen et al [63] have explored the RF sputter MgZnO thin film and tuned the sensing property by doping concentration in order to reduce the screening effect as self-powered photodector. They observed 100% enhancement in the output current and voltage of photosensor and 6-fold enhanced sensitivity compared to ZnO, which was attributed to enhanced piezoelectric coefficient for higher doping concentration of Mg in ZnO. Furthermore, Shiau et al [64] reported enhancement of the photosensitivity by 20% under the applied strain of 0.29% from MgZnO thin film-based flexible photosensors for the detection of the UV-B light. Thus, the output power of photonic devices like
photosensor, light-emitting diode, and solar cells can be enhanced by enhancing the piezotronic property of ZnO and appropriately adjusting the strain in a device.

5.6. ZnO-based piezo-phototronics for water splitting

Energy is a fundamental need for civilization to grow, but the continuous CO\(_2\) emission and global warming from conventional energy sources has a severe impact on the climate change. So, research to replace the carbon-based energy is to generation of clean energy from renewable energy sources (e.g. solar/wind energy, water splitting). Water splitting is a process where water molecule is broken either by electrocatalytic or photocatalytic chemical reactions with the production of H\(_2\) and O\(_2\) by hydrogen/oxygen evolution reaction (HER and OER) with 237 kJ mol\(^{-1}\) of energy (~1.23 eV) required. Photoelectrochemical (PEC) water splitting is a common approach for the conversion of the solar energy to chemical fuels where the photoexcited holes produce oxygen from OH\(^-\) ions at photoanode (OER) and photoexcited electrons reduce H\(_3\)O\(^+\) to H\(_2\) at photocathode (HER).

The candidate semiconductor materials suitable for water splitting materials are those having band gap higher than 1.23 eV and first demonstrated by using TiO\(_2\) as phototodecatalytic and Pt as counter electrode [65]. Attempts have been made to improve the water splitting efficiency since then, such as heterostructural materials (ZnO/ NiO \(_x\) or TiO\(_2\)/ ZnO NWs) [66, 67]. To reduce the recombination rate of the photo-generated carriers, piezo-phototronic effect in producing piezopotential upon external forces has been justified to be effective to enhance the piezo-catalytic reactions in ZnO based materials.

ZnO has attracted huge attentions as a water splitting material due to higher electron mobility (205 cm\(^2\) V\(^{-1}\) s\(^{-1}\)), longer minor carrier diffusion length, higher defect density, large surface area and effective charge transport. It is also possible to engineer the band gap and defect concentration in ZnO by doping or annealing. Recently Commandeur et al [68] reported the growth of vertically-aligned ZnO NR arrays with high surface defect density by microwave, allowing to achieve high performance with a 2-fold increase in PEC efficiency to 0.31% with a photocurrent density of 0.705 mA cm\(^{-2}\) at 1.23 V in comparison to Na-doped ZnO [69] and hydrothermally synthesized ZnO NRs [70, 71]. Furthermore, the photocurrent density (0.85 mA cm\(^{-2}\)) was increased slightly by Sb-doped ZnO, but drastically enhanced to 1.08 mA cm\(^{-2}\) under a 0.6% tensile strain by piezo-catalytical effect, which is ~27.4% higher than that without strain as shown in figure 19 [71]. Figure 19(e) shows the tensile strain increases the downward band bending at the interface, promoting the separation the electron–hole pairs and enhancing the PEC performance by the piezotronic effect. Similarly, under the compressive strain, the ZnO surface would generate negative piezopotential which would lead to upward band bending and degrade the HER/OER reactions.
In contrast to noble metals (e.g. platinum) commonly used as catalysts [72–75], Li et al [67] utilized piezocatalytic effect to enhance OER reactions by deflecting Ni(OH)$_2$-decorated ZnO heterostructure where the PEC performance is improved due to the generation/enhancement of the piezopotential at the ZnO/Ni(OH)$_2$ interface in figure 20. The strain dependent $J$–$V$ curve of the ZnO/Ni(OH)$_2$ (Na$_2$SO$_3$ as the electrolyte) revealed strain induced current increased from 0.482 mA cm$^{-2}$ (unstressed) to 0.654 mA cm$^{-2}$ (0.1%) and 0.740 mA cm$^{-2}$ (0.2%) at a bias of 1.5 V corresponding to the enhancement of $\sim$36% and $\sim$85%, respectively. The current density is further increased by the application of light illumination. Similar results on HER using piezocatalytic effect were obtained for the heterostructure of TiO$_2$/ZnO NW arrays [66].

5.7. Energy harvesting using ZnO based PENGs

Energy harvesting from minute mechanical vibrations, biological movements such as human muscle stretching, deformations is of importance as a green energy source but promising for self-powered devices. Wang et al [76] have developed both DC and AC PENGs to convert nanoscale mechanical energy to electrical energy by using ZnO NWs by applying external forces through atomic force microscope (AFM) tip. In DC PENGs, the pizopotential created by the external force overcome the SBH in the forward bias conditions when the AFM tip scans over and bend an ZnO NW, inducing the current flow through the NW. AC PENGs were demonstrated in 2009 [77] based on cyclic stretching-releasing of a ZnO fine-wire with metal electrodes at two ends as Schottky contacts, laterally bonded and packaged on a flexible substrate. The ZnO NW develops a piezopotential along the c-axis of the NW upon strain, driving electrons flow through the external circuit until reaching equilibrium. As soon as the strain is released, the piezoelectric potential
vanishes driving all these accumulated electrons flow in the reverse direction. The NW acts as a ‘capacitor’, which drives the back/forth flow of the electrons in the external circuit, resulting in an AC output.

In order to enhance the performances of PENGs, searching for new materials with higher piezoelectric coefficients is the most straightforward approach. Alternatively, it will be more beneficial and effective if the piezoelectric properties of well-developed materials could be enhanced simply by modifying the microstructure. Rivera et al found that the longer the ZnO NWs or the lower the carrier concentration, the higher the current generated in response to a mechanical deformation[78]. Riaz et al reported that the performance of the PENGs exhibits positive dependence on the aspect ratio of the NWs until 80 by both Finite element simulations and experimental results[79]. Thus, ZnO NRs with relatively small sizes and high aspect ratios are ideal for harvesting piezoelectricity due to their high bending flexibility.

Despite the interesting piezoelectric features of semiconducting NWs, free carriers in semiconductors, unlike in insulating piezoelectric materials, partially screen piezoelectrically generated immobile charges. Therefore, doping has been revealed as a distinctive strategy for improving the efficiency of energy harvesting[80–82]. Chang et al showed much higher piezoelectric output current than pure ZnO NWs by p-type doping with Li[81]. Shin et al demonstrated the increased output performance of the PENGs by enhanced piezoelectric coefficients through spontaneous polarizations in poled Li-doped ZnO NWs due to induced ferroelectricity[82].

Besides ZnO NWs, 2D NSs have also been explored for PENGs due to its exceptional high surface-to-volume ratio, and good mechanical stability for energy conversion. Moreover, Verma et al presented a flexible PENG based on vertically-aligned 2D ZnO nanodiscs in 2020[83] where thermal annealing promotes the output voltage and current density to 17 V and 150 nA cm\(^{-2}\), approximately 8 times higher than those of the pristine PENG as shown in figure 21, attributed to the passivation of ZnO surface during annealing. They also observed DC output voltage and current, which may be due to the presence of OH\(^-\) ions, restricting the back flow of electrons.

Kim et al reported DC PENGs based on ZnO NS arrays on flexible Al substrates using hydrothermal methods with a high DC power density of 11.8 mW cm\(^{-2}\) achieved under the force of 4.0 kgf[84]. The nature of DC NG with high output performance was attributed to the combined effects of buckling behavior of the ZnO NSs, a self-formed anionic nanoclay layer and coupled semiconducting/ piezoelectric properties of ZnO NSs. Wang et al also reported DC output from PENGs comprised of either 1D ZnO NRs or 2D ZnO NSs[85], where the 2D NSs PENGs demonstrated better output performance than 1D NWs PENGs, surprisingly increased from 40 nA to 0.15 \(\mu\)A under the same compressive force of 1 kgf. They attributed the DC output signals to the presence of mostly tilted ZnO NWs and the direct compression of vertically-aligned ZnO NWs.

The construction of p-n heterojunction turned out to be another key in enhancing PENG performance. Yin et al obtained an enhanced and DC output in a ZnO/NiO p–n heterojunction PENG, where the DC output voltage was up to 430 mV and the maximum output current density was of 40 nA cm\(^{-2}\), which are 21-fold higher voltage and 13 times larger current density in comparison to the pristine ZnO PENGs. The amplification is due to screening effect suppression by the p-type NiO, reduction of total capacitance and
forming p–n junction for holding charges from leaking [86]. The DC electricity implies the back flow of accumulated electrons from the bottom electrode to the top electrode is forbidden probably due to electrostatic force or electron capture by interface defects and recombination with the high-density holes in NiO layer. Wang et al also obtained DC output by forming n- ZnO NRs/p-CuO thin film heterojunction, though the output current is up to 1200 nA, 25-fold higher than that of the ZnO-based PENG [87].

6. Summary and perspective

In summary, among the various piezoelectric semiconducting materials, ZnO and its family emerged as promising candidates for developing piezotronics and energy nanogenerators due to natural abundance, low temperature facile synthesis on diverse substrates, versatile morphologies in 1D and 2D nano materials. Accordingly, a huge array of ZnO-based piezotronic devices have already been developed, where by merging the piezoelectric and semiconducting properties of ZnO, it has become possible to modify the SBH or build-in potential of a Schottky or p–n junction diode or field effect transistors through piezopotential generation under different strain conditions. In all applications, strain-induced piezopotential in semiconducting piezoelectric materials is pivotal, nonetheless, influenced by free carriers through screening effect. In principle, the higher piezopotential and less screening effect favors the power generation especially for AC mode. However, the intricate coupling of immobile piezocharges and mobile free carriers in semiconductors under stressing offer great dimensions to optimize the related SBH to achieve the promising interaction through electrostatic forces between piezopotential, gating effect and screening effect for all self-powered piezotronics. Therefore, the wise manipulation of free charge carriers and screening effect under stress renders ZnO piezotronics additional functions over multiple sensors applications like biosensors, gas sensors, humidity sensors etc. Besides, piezotronic effect can also enhance the performance of water splitting as piezocatalyst and photodetector as piezophototronics, which dictates the vital role of piezotronics in the upcoming diverse areas of human life. Nevertheless, more advancements in the technologies related to material or device-levels are still imminent to push forward for commercialization in the future. The material-level strategies drive toward further enhancing high piezoelectric tensors, including but not limited to in search of new materials, microstructure modulation, such as doping and introduction of pores, as well as more sophisticate surface functionalization. Comparatively, more strategies can be designed for the device-level strategies involving the integration of different materials with diverse functions to generate signals by interacting or coupling with humans or any matter of the interest in the environment. In current review article, we have highlighted piezoelectric semiconducting ZnO materials and its versatile applications for multiple self-powered sensors, piezotronic device and energy harvesting, which would shed light on further development of piezoelectric devices with high performance for energy harvesting, electronic skin, pressure imaging and self-powered multiple type of sensors.
Data availability statement

No new data were created or analysed in this study.

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