Device Based on Polymer Schottky Junctions and Their Applications: A Review

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ABSTRACT
Polymeric materials are emerging as an important component for organic electronics due to their combined features of soft materials and organic semiconductor/conductor. Different from solid-state bulk materials, polymers are synthesized and modulated with a facile method, with their controllable properties. Therefore, polymers have been recently used in Schottky junction devices that demonstrate features of enhanced performances, flexibility, and easy processing. Polymer-based Schottky junctions have drawn a lot of interest in several prototype applications like photodetectors, energy harvesters, and gas sensors. With this review, we summarize recent progress in synthesis and modulation of polymers and fabrication of polymer-based Schottky junction devices. Designs of applications of sensory devices like photodetectors, energy harvesters, and gas sensors are also presented.

INDEX TERMS
Polymer, Schottky junction, photodetector, energy harvester, gas sensor.

I. INTRODUCTION

In recent years, increasing interest has been devoted to inorganic/organic hybrid materials and devices because the conventional inorganic silicon-based electronics cannot avoid drawbacks like rigid systems, complicated microfabrication process, and high commercial cost [1]–[3]. Polymers are a class of organic materials that can be considered as an excellent solution to this issue due to their unique characteristics, easy processability, and commercial availability [4]–[6]. Compared with traditional solid-state brittle bulk materials, polymers combine the features of soft materials and organic semiconductor/conductor [7]. Some nature-derived polymeric materials, such as lignocellulosic biomass, offer features like renewable natural abundance, low cost, biodegradability, and ease in modifications for "green" electronics [8]–[10].

The excellent virtues of polymeric materials have enabled their incorporation into new classes of Schottky devices. Schottky junction has been extensively researched because of its weak charge storage effect, high sensitivity, and simplicity and gained its wide applications in diodes, varactors, field effect transistors, sensors, solar cells, and terahertz frequency multipliers and mixers [11]–[14]. Conventional Schottky junction relies on the contact between inorganic metals (e.g., Pt, Au, Al, Pd) and semiconductors (e.g., GaAs, ZnO, TiO$_2$) due to the higher electron mobility than organic materials [15]. Silicon-based Schottky devices have been researched in photodetectors because of their fast response and low noise and wide-gap semiconductors are always used to improve detecting efficiency [16]. In addition, one dimensional (1D) structures of metal oxides possess advantages of high surface to volume ratio and deep level surface traps [17]. Considerable attention has recently been attracted by two-dimensional (2D) semiconductors for building Schottky junctions [18]. Graphene is preferred due to its variable work function, fast carrier transit, mechanical flexibility, and optical transparency [19]. Inserting interfacial layer (e.g., BN, SiO$_2$, or insulators) enhances barrier height and rectification ratio of the Schottky junction, which is helpful for enhancing performances in electronic and optoelectronic applications [20], [21].

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methods and property degradation caused by the treatment process [22]–[25]. However, as an promising alternative, polymeric materials can be synthesized with facile methods that possess great ease and tunability, and show excellent biocompatibility, controllable electrical conductivity, enhanced mechanical properties, and possibility of low-cost large-scale fabrication [26], [27]. As a result, polymeric materials like (polyaniline (PAni), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT:PSS)) have gained remarkable advances in various fields including energy storage and conversion [28]–[31], various sensors [32], [33], and biomedical engineering [34].

Owing to the facile synthesis approach and highly controllable properties, polymers have been utilized in Schottky junction devices as an alternative of conventional inorganic semiconductive/conductive materials in the field of photodetectors, energy harvesters, and gas sensors, as shown in Fig. 1 [35], [36]. Polymer-based Schottky junction devices demonstrate excellent electrical characteristics, improved stability under ambient conditions, and large-scale fabrication [37], [38]. For example, since polymers typically are prepared in solutions through chemical or electrochemical polymerization, they can be directly spin coated or printed onto the substrate without requiring regularity at atom level, avoiding expensive equipment and complicated time-consuming fabrication process [39]–[42]. Therefore, polymer-based Schottky junctions have been applied in various fields such as solar cells, sensory devices, light-emitting devices, photodetectors, and energy harvesters for their advantages in good rectifying properties, improved performances, and easy processing and modifications.

In this review, we are going to summarize recent progress in the material synthesis and modifications, device designs, and novel applications of polymer-based Schottky junction devices. We start from the synthesis and modifications of polymeric materials and polymer-based Schottky junctions, and critically emphasize the typical applications in photodetectors, energy harvesters, and gas sensors. Moreover, main challenges about the future research are also discussed.

II. POLYMER: SYNTHESIS, PROPERTIES, AND MODIFICATIONS

Polymers are a class of unique organic materials synergizing the advantages of conductors/semiconductors and soft materials [43], [44]. In this section, we will review the facile synthesis and unique properties of polymeric materials in detail that favor their applications in the novel polymer Schottky junction devices.

A. SYNTHESIS OF POLYMERS

Generally, polymerization of monomers through chemical and electrochemical process involves oxidation, proton coupling and eliminating process [45]. Novel methods like doping engineering-enabled supramolecular self-assembly has emerging as an easy, efficient, and straightforward template-free approach for the nanostructured polymers, which possesses extra unique mechanical characteristics and electrochemical activity [46], [47]. During the doping process, redox charges are supplied to the polymer through charge injection, and dopant molecules play an important role in modulating the morphology due to the interactions between polymer chains, like electrostatic interaction, cross-linking, and steric effects [48]. By utilizing dopants with different counterion molecules that also functioned as cross-linking gelators, the morphology of PPy were effectively controlled based on the self-sorting mechanism. With the different sizes of dopant molecules, the synthesized PPy demonstrated nanostructures varying from granular particles, nanoparticles necklaces to nanofibers [49]. The controllable morphology further influences the electrical and mechanical properties of the materials [50]. This facile method can be extended to the synthesis of other polymer materials with porous nanostructures [51], [52].

In addition to the modulation of morphology, the solution-based synthesis of polymeric materials is beneficial for the large-scale and patterned fabrication of the devices [53], [54]. Typically, polymers (e.g., PAni) are prepared by mixing solutions containing monomer with acid dopant and oxidative initiator. We prepared a PPy hydrogel by using a multiphase reaction (organic phase and water phase), which was able to be casted over a large area for a uniform film [55]. This approach is highly tunable and versatile as it offers great convenience in controlling the dopant molecules and doping level that affect the morphology and properties of polymers [51], [56]. Moreover, such a solution-based synthetic method can introduce new functions to polymers [57]. In order to obtain micropatterned electrodes and large-scale fabrication of array, the synthesized polymer hydrogels can be processed through solution-processing techniques like spray coating, spin coating, inkjet printing, and screen printing due to its high content of water as well as suitable solubility and viscosity [58], [59]. Compared with
TABLE 1. Fundamental parameters of polymer-based Schottky junctions and inorganic junctions.

| Conductor   | Work Function (eV) | Semiconductor | Work Function (eV) | Barrier Height (eV) | Ideality Factor | Rectification Ratio | Ref. |
|-------------|--------------------|---------------|--------------------|-------------------|-----------------|---------------------|------|
| PEDOT:PSS   | 5.52               | TiO₂          | 0.71-0.86          | 2.89-4.14         | 150             | [86]                |
| PEDOT:PSS   | 5.1                | CuO           | 0.726              | 1.68              | 10              | [87]                |
| PEDOT:PSS   | 5.52               | ZnO           | 0.46-0.85          | 1.7-2.2           | [88]            |
| PEDOT:PSS   | 5.0                | ZnO           | 0.9                | 1.4               | [24]            |
| Al          | 4.28               | PEDOT:PSS     | 5.16               | 0.6               | 3.37            | $1.3 \times 10^4$   | [37] |
| PAni/poly-3-methyl thiophene |       | Si            | 4.2               | 0.334             | 2.24            | 100                 | [93] |
| Al          | 3.7-4              | GaN           | 1.2               | 1.23              | [89]            |
| Ti          | 4.28               | PPy           | 4.1-4.28           | [90]              |
| Ag NW/ITO   | 4.09               | PPy           | 4.42-4.49          | 0.5               | 1.11            | [73]                |
| Pr          | reduced graphene oxide | Si            | 0.73               | 1.58              | [91]            |
| MWCNT       | 4.8                | ZnO           | 4.2               | 0.534             | 2.24            | 100                 | [93] |
| Al          | Si                 | 0.69          | 3.89              | 103               | [94]            |
| Graphene    | 4.6                | ZnO NW        | 4.7               | 0.28              | 1.7             | [95]                |

traditional complicated device fabrication process involving photolithography and metal deposition, these techniques allow low-temperature fabrication of devices, avoiding the formation of interfacial trap states and property degradation caused by the thermal, light, and chemical corrosion.

B. MECHANICAL AND ELECTRICAL PROPERTIES OF POLYMERS

Excellent mechanical properties of polymeric materials are expected for complicated, free-standing structures and robust performances in the applications of flexible and stretchable electronics [46]. The solution-based synthesis method of polymers also enables simple and effective integration with other nanoscale materials such as metal/metal oxide nanoparticles and carbon nanomaterials (graphene and carbon nanotubes) [60]. The incorporated materials help improve the temperature and mechanical stability due to the hierarchical nanostructures [47], [61]. For example, treating PEDOT:PSS using mild acids instead of strong acids increases the mechanical flexibility and stability for organic solar cell applications [62]. Introducing plasticizing additives such as Zonylfluorosurfactants or ionic liquids to PEDOT:PSS can render this material mechanically stretchable to enable the applications in stretchable circuits, bioelectronics, and flexible electronics [56], [63], [64]. It is explained that the additives that also function as dopants weaken the interactions between PEDOT and PSS domains and lead to charge delocalization and transport and increased crystallinity/molecular order [65], [66].

In addition, the additives are beneficial for the property improvement of the polymer materials. Since polymers are pure conductivity material, the introduction of conductive materials will construct a hybrid framework and improve the conductivity of the polymeric system [67]. By adding dodecyl benzene sodium sulfonate (DBSS), it was reported that a kind of PEDOT:PSS enhances its conductivity as high as 700 S cm$^{-1}$ and tolerates strain over 100% [56].

Since the carrier concentration plays a significant role in determining the junction properties and device performances, the features of controllable electrical properties of polymers make them an excellent candidate for Schottky junction devices [68], [69]. Taking PAni as an example, its intrinsic conductivity is determined by the polymer protonation that is related to doping level and strength. PAni can transfer between the emeraldine base (EB) and emeraldine salt (ES) forms, realizing a reversible transition in its electrical conductivity from insulator, semiconductor to metallic conductor as well as optical band gap energy [70], [71]. With the controllable electrical properties, polymers have been an important alternative of silicon and other inorganic materials as metallic conductors or semiconductors [72]. As shown in Table 1, intensive attempts have been made to use different types of polymers (e.g., PAni, PPy, PEDOT:PSS, polycarbazole, and polythiophene) to construct Schottky diodes that can be formed between the metal/polymer or metal oxide/polymer interface [73]–[75].

In addition to chemical modulation in conductivity, electrical properties of polymeric materials are also sensitive to physical deformation. For example, based on the mechanochemoelastic (MCE) effect of free-standing polymer film [76], the mechanical energy can be transformed into electrical energy, and the induced charge within the polymer was observed to be related with the strength of load, the dimensional change of the film, and the doping level of the material. This effect was explained by the stretching of main chain and the change of the density of state near the chemical potential. This unique electromechanical coupling has been applied in the devices including mechanical sensors, energy generators, and actuators [77], [78]. The reverse actuation in PPy was observed where 1000 C m$^{-3}$ charge was generated
under 1% strain [79]. According to the “deformation induced ion flux” mechanism they proposed, the volume change caused by the applied strain influence the ion concentration and result in a separation of charges in the polymer, leading to the voltage generation. It was proved for the first time that this behavior occurs in microsized devices based on PEDOT:PSS, and the microdevices even demonstrated a higher mechanical sensitivity (0.74 mV/%) than thick macroscopic counterparts [80].

C. POLYMER-BASED SCHOTTKY JUNCTIONS

For inorganic devices, metal deposition and surface treatment tend to cause irreproducible properties and performance degradation, whereas the introduction of high-quality soft polymers can be a good solution to these drawbacks [81]–[83]. In addition, devices in the form of Schottky junction possess advantages in solving drawbacks, such as poor stability, mechanical properties, and non-homogeneity of the pure polymer devices. Introducing modified polymer composites or controlling the polymer-metal or polymer-semiconductor interface may help improve diode properties and mechanical and thermal stability [50]. Table 1 lists typical polymeric materials involved in Schottky junction devices along with their representative parameters. For instance, PANi has been researched in Schottky diodes due to simple oxidative synthesis and non-redox doping in acids. PEDOT:PSS has apparently been one of the most commonly used polymers in Schottky diodes for its features of large work function (5–5.2 eV), high conductivity, and high transmittance in a wide wavelength range (250–800 nm) [84], [85].

Polymers can be used as either conductors or semiconductors in Schottky diodes due to their easily controlled electrical conductivity. Typically, Fig. 2a shows the formation of Schottky contact based on a p-type polymer semiconductor. When the polymers are in contact with metals with a lower work function, a Schottky junction will be formed at the interface. Otherwise, metals with higher work function will form Ohmic contacts (Fig. 2b) [96], [97]. For n-type semiconductors, the situation is a reverse. Schottky contact is formed with metals having higher work function, whereas Ohmic contact is formed with metals with lower work function. For conductive polymeric materials, metal oxide nanoparticles or nanorods (NRs) are often used to build Schottky contact due to their compatibility in the soft material processing and device fabrication.

To characterize the polymer-based Schottky junction devices, several important parameters that significantly affect the device performances are summarized in Table 1. Similar to traditional inorganic Schottky junctions, the rectifying behavior of the polymer-based device follows the thermionic emission theory [98], [99]. The barrier height (ΦB) can be evaluated as

$$\Phi_B = \left(\frac{kT}{q}\right) \ln \left(\frac{A^* T^2}{I_S}\right)$$

where A and A* are the contact area and the effective Richardson constant, respectively. T, k, q, and I_S represent the absolute temperature in Kelvin, the Boltzmann’s constant, the elementary charge, and the reverse saturation current, respectively [100]. The relation between the current density and voltage goes as

$$J = J_0 \exp(qV/\eta kT) - 1$$

where J and J_0 represent the current density and the reverse leakage current density, respectively [90]. The ideality factor (η) is calculated by

$$\eta = \frac{q}{kT} \frac{d(V)}{d(\ln I)}$$

where I and V represent the current and applied bias voltage, respectively [24]. For an ideal Schottky diode, η = 1.

It was proven that utilizing polymeric materials in Schottky diode gives rise to good rectifying properties, which provides an alternative for high-performance devices. For instance, a high-quality Schottky junction based on conducting PEDOT:PSS and ZnO single crystal was fabricated, demonstrating a high rectification ratio (∼107) and small ideality factor (1.2), which was comparable to the best of devices based on Ag and Pt electrode at that time [75], [101], [102]. Polycarbazole, a thermally stable p-type semiconductor polymer, was used in a polycarbazole/Al junction device that demonstrated good rectifying nature with a barrier height of 0.85 eV and ideality factor of 1.9 [72]. The extremely low reverse saturation current was beneficial for its applications in optical detection with low noise. Polymeric blend (PAni/poly-3-methyl thiophene)/p-Si/Al structure was also proposed for a Schottky junction that possessed an ideality factor of 3.37 [39]. It was explained that the higher value of ideality factor was attributed to the interface states, interfacial layer, and series resistance [103]–[105].

In addition to the performance enhancement, introduction of polymeric materials is beneficial for the control and modifications of junction properties of the Schottky contacts. For example, the morphology of the polymeric materials affected the performances of the device. Schottky diodes

![FIGURE 2. Band diagram showing the formation of p-type semiconductive polymer-based Schottky contact (a) and Ohmic contact (b).](image-url)
based on electrospun PANi nanofibers with thicker diameters possess clear rectification behavior, whereas decreasing the diameter of fibers significantly reduces the rectification ratio [106]. The electrical characteristics of these devices based on polymers are often affected by the doping process [90], [107], [108]. Dopant type has an influence on the Fermi level of the semiconductive polymer and hence affects the rectifying behavior of the Schottky junction device [109]. The properties of polymer-based Schottky diodes are influenced by the counter ions of the supporting electrolytes during the synthesis, which may be due to the dopability of the polymer, the morphology, and the mobility of carriers in junction [100]. When comparing the junction properties of Al/PAni contact, where the polymer was doped with different-sized and structurally-related dopant anions, it was found that the junction based on PANi doped with methane sulfonate anion (MSA) had a rectification ratio four times higher than that doped with sulfate anion (SA) [110]. Moreover, the effect of inserting different kinds of hybrid polymer/metal multilayers on the performances of Au/p-Si Schottky junction was studied [111]. Interestingly, it was found that the types of the polymer/metal hybrid materials and their thickness were able to tune the barrier height and ideality factor of the Schottky junction [112].

III. APPLICATIONS OF POLYMER-BASED SCHOTTKY JUNCTIONS

Based on unique controllable properties as well as the facile preparation and processing of polymeric materials, polymer-based Schottky junction devices have demonstrated enhanced performances and properties compared with conventional inorganic devices. Therefore, great potentials have been demonstrated in various fields such as photodetectors, energy harvesters, and gas sensors. In this section, we are going to emphasize the applications of polymer Schottky junctions from the aspect of device fabrication and design and performance optimization.

A. PHOTODETECTOR

Polymeric conductors and semiconductors are often preferred in organic solar cells, transistors, and photodetectors for their controllable electrical properties, high transparency, and potentials for flexible electronics [113]–[117]. For example, PANi was spin coated on a silicon wafer to form a heterojunction for detection of ultraviolet (UV) [118]. Poly(3-hexylthiophene) (P3HT), a kind of p-type semiconductor, was utilized with ZnO NRs to fabricate a hybrid photoanode that demonstrated a high photoconversion efficiency and stability [119].

Schottky junction devices are considered as an excellent candidate for photodetectors due to its supersensitive and ultrafast response, low power consumption, vertical structure, and ease in fabrication [120]–[123]. For example, a one-dimensional (1D) patterned polymer with donor–acceptor configuration was employed in organic photodetectors, which demonstrated excellent optoelectronic performances with a high on/off ratio and responsivity [124]. A self-powered, vertically structured Schottky diode was developed based on Al-doped MgZnO and PEDOT:PSS, which possessed low dark current because of the high electron concentration and crystalline quality in the MgZnO film (Fig. 3a and 3b) [125]. The device demonstrated a peak responsivity of 19.1 mA/W attributed to the low resistivity of MgZnO and good Schottky contact (Fig. 3c). Possibility in the array integration for UV imaging and sustainability due to the self-powered property are also attractive for practical applications.

As a general mechanism of hole-trapping in photodetector, when a Schottky contact is formed at the interface of n-type metal oxide semiconductor and conducting polymer, there is a depletion layer at the junction as a result of the accumulation of electrons (Fig. 4a). Upon illumination of light, electron–hole pairs will be generated, among which the holes migrate to the interface because of the band bending and electrons are collected to increase the photocurrent (Fig. 4b). The barrier height is reduced and the depletion region shrinks, which favor the extra carrier injection and electron tunneling. Different from p-n junction, the carriers are generated directly in the barrier region of the Schottky junction, which greatly reduces the response time and recombination during the diffusion [126].

![FIGURE 3.](image-url)  
(a) Schematic illustration of PEDOT:PSS-based photodiodes; (b) Microscope image of the photodiodes; (c) Spectral response of the photodiodes. Adapted from [125] with permission, copyright 2016 IEEE.

![FIGURE 4.](image-url)  
Mechanism of hole-trapping used in a photodetector based on a Schottky junction formed by n-type semiconductor and conducting polymer.
Table 2 lists comparisons of performances of photodetectors based on polymer-based Schottky junctions and inorganic junctions. To improve the sensing performances of the organic devices, a UV detector was fabricated based on ZnO and two kinds of hole-conducting semiconducting polymers through a solution-based process (Fig. 5) [127]. The photodetector showed a high responsivity of \( \sim 721-1001 \, \text{A} \cdot \text{W}^{-1} \), which was up to three orders higher than that of the existing inorganic devices. A ZnO NRs/PEDOT:PSS Schottky diode was designed for visible-blind UV detection (Fig. 6a and 6b) [99]. The conducting polymer was spin-coated onto the NRs so as to improve the photocurrent. The hybrid organic/inorganic system demonstrated a rectification ratio of 43 at \( \pm 1 \, \text{V} \) bias and an external quantum efficiency (EQE) over 100%. Interestingly, graphene quantum dots were introduced to promote generation of electron--hole pairs, resulting in the hole trapping and suppressing carrier recombination for the superior photoconductive behaviors [128]. The modified junction enhanced its rectification ratio to 56 at \( \pm 1 \, \text{V} \) bias. In addition, by treating the PEDOT:PSS polymer with acid (e.g., dimethyl sulfoxide (DMSO) and concentrated H\(_2\)SO\(_4\)), its electrical conductivity will be enhanced, resulting in a higher EQE (\( \sim 12560\% \)) and responsivity (\( \sim 34.43 \, \text{A} \cdot \text{W}^{-1} \)) as well as faster response and recovery (Fig. 6c) [86]. Due to the improvement of the conductivity, the series resistance of the device is reduced and the carrier transport is promoted at the junction [129].

### B. ENERGY HARVESTER

Tactile sensors realizing mechanical-to-electrical energy conversion have shown significant potentials as renewable energy sources in various fields including self-powered electronic skin, portable small-scale electronics, wearable healthcare monitoring, and intelligent human-machine interface [134]–[137]. Energy harvesters like triboelectric nanogenerator (TENG) and piezoelectric nanogenerator (PENG) typically generate alternating current (AC) voltage, whereas Schottky junction-based harvesters can directly convert mechanical energy into continuous direct current (DC) signals, which is beneficial for applications in self-powered devices without requiring rectification [138]–[141].

### TABLE 2. Performances of photodetectors based on polymer-based Schottky junctions and inorganic junctions.

| Material       | Wavelength (nm) | Responsivity (A/W) | Detectivity (Hz\(^{1/2}\)/W) | Response Time | Ref. |
|----------------|-----------------|--------------------|------------------------------|---------------|-----|
| Al:MgZnO/PEDOT:PSS | 278             | 0.02               | 3.20\times10\(^{11}\)       | 0.3 s         | [125]|
| PDDBT-T1       | 532             | 3.24               | 5.4\times10\(^{11}\)        | 0.85 s        | [124]|
| P3HT/ZnO       | 360             | 721-1001           | 1.3\times10\(^{12}\)        | [127]         |
| ZnO/PEDOT:PSS  | 340             | 36                 | 6.3 \times 10\(^{4}\)       | 0.18 s        | [99] |
| CuO/PEDOT:PSS  | 300-700         | 0.3                | 1.6\times10\(^{11}\)        | 0.5 s         | [87] |
| TiO\(_2\)/PEDOT:PSS | 380         | 34.43              | 134.8                        | [130]         |
| Au/TiO\(_2\) nanorod | 350         | 70                 | 600 s                        | [19]          |
| TiO\(_2\)/Ag    | 380             | 3                  | 2.53 \times 10\(^{8}\)      | 0.3 s         | [131]|
| TiO\(_2\)/p-Si  | 325             | 0.46               | 3.2 \times 10\(^{9}\)       | 0.7 s         | [132]|
| graphene/Ge     | 1550            | 70                 | 600 s                        | [19]          |
| p-ZnTe/In       | 550             | 10.9               | 69 \mu s                     | [133]         |
To obtain DC signals, a Schottky nanocontact by sliding a conductive microscope tip on a molybdenum disulfide (MoS$_2$) thin film demonstrated a current density up to 106 A·m$^{-2}$ [140]. A hybrid PENG based on ZnO nanosheets/Au Schottky junction showed a high DC output of 0.378 V [142]. The working mechanism was that the applied mechanical pressure separated the charges, causing the charge accumulation and band structure change of the ZnO. A unique moving Schottky diode was developed based on graphene/metal and semiconductor. The DC signals were generated by moving graphene or metal on the semiconductor substrate, which achieved an output density of 40.0 A·m$^{-2}$ (Fig. 7a) [143].

It was explained that the dynamic appearance and disappearance of the depletion layer in the junction caused the separations of the drifted charges and generated electric power output that is 100-1000 times higher than former TENG and PENG. Using graphene as the metal material can improve its flexibility and lifetime as a result of its high conductivity and flexible mechanical properties, which benefits its application as a wristband with a continuous DC voltage output (Fig. 7b and 7c). Different from static Schottky junction, the electrons and holes in dynamic Schottky diode do not need to cross over the junction and the carriers can be rebounded back by surface states. Therefore, by increasing the surface states, the current density was further improved to 2.7 $\times$ 10$^9$ A·m$^{-2}$ because the carriers were accelerated due to the large atomic electric field and the reflecting direction was regulated by the built-in electric field [144]. These Schottky junction-based energy harvesters require no additional rectification circuit and favors the miniaturization and integration of the electronic devices, providing a new route for the self-powered devices and mechanical sensors [123].

Introduction of soft polymeric materials into energy harvesters will enable higher electric output and broaden their applications in flexible devices [79], [145], [146]. It was confirmed that Schottky contact was formed between p-type semiconductor PPy and metal Al and Ohmic contact was formed between the Au and PPy (Fig. 8a and 8b) [147]. They adopted a sandwiched structure with a free standing polymer thin film between two metals, which generated DC power under compression with a voltage of 0.7 V and current density of 62.4 $\mu$A·cm$^{-2}$ (Fig. 8c). It was explained that the barrier potential of PPy/Al Schottky contact was reduced due to the compression, facilitating the carrier movement to the metal side [148]. The charge density in PPy was also increased due to the compression of physical volume. The Schottky junction itself played an important part in the directional transfer of electrons and hence contributed to a DC output. Similarly, other semiconducting polymer (e.g., PANi and PEDOT:PSS), and metal oxides (e.g., SnO$_2$, Al$_2$O$_3$, and ZnO) were also able to in the DC generators based on polymer–inorganic oxide junction [149]. In addition, by doping the polymer with acids, the electric outputs of the DC generators can be further enhanced because of the decreased barrier height, shorter interchain distance, higher charge density, and reduced internal resistance (Fig. 9) [150]. For example, the device utilizing PANi doped with HCl generated higher output (0.9 V and 33.9 $\mu$A·cm$^{-2}$) than that made from undoped PANi (1.5 mV and 0.55 nA·cm$^{-2}$). The barrier height decreased to a larger extent under compression for the doped polymer. The smaller sized dopant molecule can lead to shorter interchain distance, which changes consistently with the modulus value and electrical resistance and decides the energy conversion property of the device. Introduction nanoscale materials like graphene oxide and carbon nanotube into polymeric materials can increase the output current up to 1.319 A·cm$^{-2}$ and power density up to 0.21 W·m$^{-2}$, because the nanomaterials further increase the charge storage and reduce the barrier height and internal resistance. Therefore, these energy harvesters demonstrate great potentials to be applied in movement sensors for the motion and force detection [151].

In addition, the piezotronic effect is another highly effective approach to enhancing the energy conversion
efficiency without complicated, high-cost microfabrication [152], [153]. As an effective interfacial regulating strategy, this effect uses piezoelectric polarization charges at the interface to achieve pressure/strain-induced modulation of other types of responses [154], [155]. It was found that external strain can improve the sensitivity of a Schottky diode-based humidity sensor, because the strain induced polarization piezo-charges at the junction [156]. Piezophototronic effect was also utilized in PEDOT:PSS/ZnO junction, which realized spatial pressure distribution mapping with a resolution of 7 μm [157]. The strain-induced charges present at the junctions modify the band structure by reducing the barrier height for charge injections and facilitating recombination. A heterostructure photosensor was constructed with a-axis GaN microwires and p-type PEDOT:PSS, of which the sensitivity and responsivity can be enhanced to 508% and 354% when applied a -0.32% compressive strain [158].

C. GAS SENSOR

Gas sensors converting the concentration of target vapors into electrical signals are widely used in detecting the hazardous gas in the environment. Inorganic material and devices such as p-n junctions and transistors have been intensively investigated for the monitoring of gases because the transistor-configured sensors exhibit great ease and efficiency in device integration, lower limit of detection, and higher sensitivity due to the amplification of devices when compared with the chemiresistors based on polymers or metal oxides [159]. For example, Pt/AlGaN/GaN Schottky junction device was reported to have a high sensitivity to NH₃, which, however, can only be achieved at a high temperature [160]. Instead, organic polymeric materials offer the possibility of room-temperature of operation and detecting a wide range of different gases [161], [162]. Therefore, there have been some impressive researches using polymer-based Schottky diodes in the gas detection, like ammonia (NH₃), nitric oxide (NOₓ), and hydrogen (H₂) [98], [163]. Table 3 lists the comparison of performances between polymer-based Schottky junctions and inorganic devices.

Based on the reversible doping/dedoping mechanism of the polymeric materials, the gas molecules adsorbed by the sensor change the series resistance and Fermi level of the polymer, and affect the barrier height of the junction [164], [165]. For example, NOₓ exhibits an acceptor behavior and can enhance the doping level in the p-type PPy, which reduces the Schottky barrier [166], [167]. NH₃ molecules act as an electron donor and decrease the charge carriers in PEDOT:PSS and PAni.

Addition of nanoscale materials to polymeric materials helps improve the responses of the gas detection. BiVO₄/polymer (PTFE, PVDF, PAni) was utilized in

### TABLE 3. Performances of gas sensors based on polymer-based Schottky junctions and inorganic junctions.

| Material          | Gas    | Working Temperature | Response | Response Time | Recovery Time | Stability       | Ref.   |
|-------------------|--------|---------------------|----------|---------------|---------------|-----------------|--------|
| PAni/Ti₃C₂T₄     | NH₃    | RT                  | 0.05-400% (0.025-50 ppm) | 7 min | 0.083 min | 88% for 35 days | [171] |
| N-GQDs/PAni/Ag    | NH₃    | RT                  | 110.92 (1500 ppm) | 30 s | 190 s | 95% for 4 months | [172] |
| Pd-PAni          | NH₃    | RT                  | 6-21 (10-500 ppm) | 95 s | 121 s | 30 days | [169] |
| PEDOT:PSS/GaAs    | NH₃    | RT                  | 92% (100 ppm) | 300 s | 2100 s | 35 days | [170] |
| PCDTBT           | NO     | RT                  | 11.5-87.2% (50-200 ppm) | 0.87 min | 277 s | 67.2% for 35 days | [174] |
| PAni/WS₂         | NH₃    | 20-100 °C           | 50-123% (10-50 ppm) | 3.1% (10 ppm) | 75 s | 600 s | 88% for 35 days | [175] |
| PAni/TiO₂/Au     | NH₃    | RT                  | 103.9 (10 ppm) | 72 s | 101 s | 98% for 30 days | [177] |
| TiO₂/Ti₃C₂T₄     | NH₃    | RT                  | 3.16% (30-500 ppm) | 3.16% (10 ppm) | 75 s | 600 s | 88% for 35 days | [175] |
| Au@ZnO           | H₂     | 300 °C              | 103.9 (10 ppm) | 75 s | 600 s | 88% for 35 days | [176] |
| Pt@SiC           | H₂     | 300 °C              | 3.16% (30-500 ppm) | 72 s | 101 s | 98% for 30 days | [177] |
Schottky diode-type sensor for detection of NH₃, N₂, and O₂ [168]. The junction performance can be rationalized by addition of graphene oxide to change the conductivity of the polymer. The sensitivity of the sensor was significantly improved based on the coupling effect between the graphene oxide nanosheets and polymers. Similarly, mixing graphene oxide with PEDOT:PSS was used to design a PEDOT:PSS/GaAs Schottky diode [169]. The functional groups on graphene oxide nanosheet cause the polymer to adsorb positive charges and results in phase separation between PEDOT and PSS chains (Fig. 10a). Therefore, active sites and carrier mobility are increased due to the PEDOT-rich domains and longer pathway. The device showed a high sensitivity of 194 to 20 ppm NH₃ and fast response and recovery (Fig. 10b). This type of gas sensor has demonstrated great potentials in high-sensitivity, high-selectivity, and high-speed applications. A flexible NO gas sensor was developed based on poly[N-9-heptadecanyl-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)] (PCDTBT) as the active material [170]. The PCDTBT polymer with good adhesion was spin coated onto the flexible substrate and the sensing performances can be improved under bending conditions, which will promote its applications in flexible electronics. Exposure to NO gas changes work function of the polymer from 5.15 eV to 5.25 eV and modulates the barrier height between the polymer and gold electrode, resulting in the current change by almost 6 times. A PANi/Ti₃C₂Tₓ hybrid NH₃ sensor exhibited outstanding sensing performances as well as air stability and mechanical flexibility resulting from the enhancement effect of the Schottky junction [171]. The sensor can tolerate humidity from 20% to 80% and temperature from 10 °C to 40 °C, making it suitable for practical agricultural applications.

In addition to the gas sensor, the polymer-based Schottky junction devices can also seek promising applications in other types of chemical sensors or biosensors because of its chemical stability and simple polymerization approach [178], [179]. These sensors are envisioned to have tremendous potentials in the industrial environmental monitoring that detects hazardous substances, and wearable, portable health assessment devices that targets metabolites related to human health status [180]. However, there have been few researches exploring these applications and much more attention and efforts are expected.

**IV. CONCLUSION**

In conclusion, this review summarizes recent progress in polymer-based Schottky junction devices and their applications in sensor devices. Starting from the polymeric materials, we review the novel synthesis, unique properties, and effective modifications of several typical polymers, and demonstrate their advantageous features and potentials to be applied in the Schottky junction devices. The following features of polymers have enabled their great potentials to be utilized in Schottky junction devices: i) Polymers are easy to synthesize by means of chemical or electrochemical polymerization and are compatible with various room-temperature large-scale, low-cost deposition techniques, such as printing methods. ii) The electrical/mechanical properties and morphology of the polymers can be modulated effectively and easily by means of doping engineering, thus regulating the properties of the polymer-based Schottky junctions. iii) The sensory devices based on polymer Schottky junctions offer comparable or better performances with those of conventional Schottky junction devices. In addition, the hybrid Schottky junction devices possess great potentials to be applied in flexible electronics based on the organic and nanostructured materials.

In spite of the progress already achieved, several challenges still remain and need to be solved before the widespread practical applications of polymer-based Schottky junction devices. First of all, the further performance improvement is always among the research hot spots. Currently, the non-crystalline and amorphous properties of the polymers make it difficult to obtain uniform and structured devices, thus affecting the performance of the device. Moreover, the flexible applications require much higher stability of the performances. Novel device structure optimization and material design will help enhance the device performances to meet the demands in real-world applications. Second, polymeric materials are considered to be an important component in next-generation flexible and stretchable electronics. However, some of the polymer-based Schottky junction devices still partly rely on the traditional bulk inorganic materials (e.g., silicon), which hinders their applications in flexible and stretchable electronics. Therefore, all organic devices with simple fabrication process are expected to render the whole system mechanical flexibility and stretchability to become an effective candidate in wearable and portable electronics. Although various methods have been developed for the synthesis of polymeric materials, more standard and precise processing technologies need to be explored for large-scale fabrication of flexible devices. Third, different types of sensory devices (e.g., electrochemical sensor and biosensor) as well as multimodal sensing function based on the Schottky junction are expected to be explored to broaden their real-world applications. For example, energy harvesting components can be integrated with other functional polymer-based devices.
sensors to construct a self-powered sensing platform with multiple purposes. Future advances in the device fabrication and optimizations are envisioned for emerging applications in various fields.

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