Metal oxide semiconductor-based Schottky diodes: a review of recent advances

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Abstract
Metal-oxide-semiconductor (MOS) structures are essential for a wide range of semiconductor devices. This study reviews the development of MOS Schottky diode, which offers enhanced performance when compared with conventional metal-semiconductor Schottky diode structures because of the presence of the oxide layer. This layer increases Schottky barrier heights and reduced leakage currents. It also compared the MOS and metal-semiconductor structures. Recent advances in the development of MOS Schottky diodes are then discussed, with a focus on aspects such as insulating materials development, doping effects, and manufacturing technologies, along with potential device applications ranging from hydrogen gas sensors to photodetectors. Device structures, including oxide semiconductor thin film-based devices, p-type and n-type oxide semiconductor materials, and the optical and electrical properties of these materials are then discussed with a view toward optoelectronic applications. Finally, potential future development directions are outlined, including the use of thin-film nanostructures and high-k dielectric materials, and the application of graphene as a Schottky barrier material.

1. Introduction
Despite the emergence of the modern semiconductor devices in the last 70 years, these have substantially revolutionized the human society [1]. The core of these devices are the physical characteristics of the semiconductor material; including its integration of electronic and optical properties which allows interaction and regulation of the photon, electrons, and holes using different electronic infrastructure and operating environments. Most studies confirm the metal-semiconductor (MS) as a prime component of the modern electronic components [2–4]. Initially, the metal-semiconductor solid-state device was discovered in 1874 and referred as whisker contact rectifier, which included a wire tip pressed onto a lead sulfide crystal. Ever since, these devices continued to capture great attention in monitoring and testing due to their low cost, high sensitivity, and simplicity [2].

The realization of the metal-semiconductor junction is needed for appropriate use of electronic devices such as diodes, varactor diodes, metal-semiconductor field-effect transistors (MESFETs), high electron-mobility transistors (HEMTs) and heterojunction bipolar transistors [5–8]. The wide range of MS junction and its application highlights is significant. Researchers have investigated different MS junctions over a long period, and hence their physics are well understood. However, there lacks a comprehensive analysis of MS junction and its use, application, and challenges in the research. To reinforce the significance of MS, this review is conducted which helps enlighten the progress that has MS junction has undergone since its initial discovery in the 1847, along with its application, use, challenges, and potential. Seol et al [9] have recognized that the contact of semiconductor with metal provides two types of the junction, namely: the ohmic junction or the rectifying (Schottky) junction. In an ohmic junction, the current (I) changes linearly with the applied voltage (V) and follows Ohm’s law [10].
Low contact resistance is required for good ohmic contact and high-speed semiconductor devices. In contrast, an ideal Schottky junction acts like an ideal diode, where high current only flows in the forward-biased direction and offers infinite resistance in the opposite direction [11]. The type of junction can be changed by varying different metals and the doping level of the semiconductor [12]. The core focus of this study is on the Schottky diode for its use in the switching devices, which reduces the current leakage and power consumption [13].

This review is categorized into five sections. Following the introductory section, the comparison of MS and MOS devices is provided in the second section, while important equations related to MOS Schottky Diode are described for carrier transport mechanism in the third section. The fourth section highlights the recent progress of MOS devices and their applications in the fourth section. Lastly, section five briefly sums up the reviewed findings and indicates the future direction of the work.

2. Review

Generally, the metal oxide/insulator semiconductor (MOS/MIS) structure is obtained by inserting an insulator layer between a metal and a semiconductor [14]. In the MOS structure, an oxide layer separates the metal and semiconductor from each other. For instance, at the metal/insulator interfaces, there is a continuous distribution of surface states with energies located in the bandgap of the semiconductor [15]. The intermediate oxide layer helps prevent the diffusion of the metal into the semiconductor but also alleviates the electric field reduction in MIS Schottky diodes. The interfacial layer helps determine the device characteristics, performance, and stability [16]. Karabulut et al [17] explains that the MOS or MIS capacitor is the most effective device for semiconductor surfaces based on their practicality, reliability as well as stability for different surface conditions. The author describes the MIS structure stating that it has a metal oxide interfacial layer with about 3, 5, and 10 nm surface thickness, the hafnium dioxide (HfO2) thin film, which grows through the use of ALD techniques.

The particular focus on the Indium Phosphide (InP) is because of its high power as well as frequency electronics given its superior electron velocity for the widely used semiconductors. It along with Gallium Arsenide (GaAs) are identified as effective fabrication material for opto- and micro-electronic devices [18].

MOS devices are compulsory for space applications, which can withstand harsh atmospheric environments with strongly ionization radiation fields and high-temperature atmospheres. The MOS structure is a compulsory part of electronic devices, such as solar cells, metal oxide semiconductor field-effect transistors (MOSFETs) and Schottky diodes [19–21].

The selection of substrate, an intermediate layer, and growth process plays a key role in determining the characteristics of Schottky barrier diodes (SBDs). Indium phosphide (InP) is an important III-V material due to its electronic and optoelectronic device applications, such as solar cells, laser diodes, photodetectors, HEMTs, high-speed metal insulator semiconductor field-effect transistors, microwave sources and amplifiers operating at high power and high frequencies [22]. The major discrepancy in using an n-InP substrate for Schottky junctions arises due to high surface states and nonstoichiometric defects, which results in lower height value (< than 0.5 eV) of Schottky barrier [23] and a high reverse leakage current [24].

Cetin and Ayylidiz [25] first studied the electrical properties of a MOS Schottky diode fabricated on an InP substrate and showed that Cu/n-InP and Al/n-InP Schottky barrier diodes with and without the interfacial oxide layer were fabricated.

Native oxides have great importance in the passivation of the InP surface. Wolan and Hoﬂund [26] investigated these native oxides on the InP surface and found that oxides, such as In(OPO3)2 condensed phosphates, can lead to MOS Schottky devices with low interface state density. Thus, minimum unsaturated bonds exist at the interface. Lima et al [27] showed that Al/TiN is suitable to use for complementary metal-oxide-semiconductor devices.

Kaufmann et al [28] studied the SiC Schottky diode as a particle detector. The authors fabricated Schottky junctions by depositing dielectric HfO2 and TiO2 insulating layers using atomic layer deposition onto a silicon carbide substrate. An increase in ideality factor and a decrease in barrier height was found with the increase in the thickness of the insulating layer for both dielectric materials. The barrier height lowering with an increase in thickness is due to the potential drop in the layer [29]. The reverse bias current characteristics for Ni/TiO2/SiC and Ni/HfO2/SiC Schottky structures are shown in figure 1.

Güçlü et al [30] showed that the Schottky barrier is obtained by inserting a thin insulator layer of Al2O3 using atomic layer deposition on a n-GaAs substrate. Table 1 presents summary of some of these studies, depending on the oxide growth and different substrates used.

The comparison of the physical properties of the semiconductors is provided in table 2 concerning Si, ultrawide bandgap (β-Ga2O3) and wide bandgap (GaN, SiC). The development of the β-Ga2O3 is based on it being cost effective, easy, and its method for mass-producible meltdown, i.e., floating zone (FZ) and the edge-
defined film-fed growth (EFG). It also presents better growth as a high quality single-crystal which makes it a potential and promising material for the semiconductor devices like Schottky barrier diode as well as metal-oxide-semiconductor field-effect transistor (MOSFET) [7, 8].

The structure of MOS (also referred to as MOS capacitor) is simple and like plate capacitors, where an oxide material is sandwiched between a metal and a semiconductor. Depending on the various applications, the basic MOS structure can act as a MOS Schottky diode, capacitor, or as a gate in MOSFET transistors [46]. The schematic diagram of a MOS structure is shown in figure 2.

Table 1. Summary of MOS Schottky Diodes.

| Substrate   | Oxide layer | Deposition method          | Metal layer | References |
|-------------|-------------|----------------------------|-------------|------------|
| P-Si        | TiO₂        | Atomic-layer-deposited (ALD) | Al          | [1]        |
| n-InP       | SiO₂        | Oxygen Plasma              | Au          | [23]       |
| SiC         | HFO₂, TiO₂  | ALD                        | Ni          | [26]       |
| n-GaAs      | Al₂O₃       | ALD                        | Au, Ti      | [30]       |
| n-In GaN    | SiO₂        | Radiofrequency (RF) sputtering | Pt          | [31]       |
| AlGaN       | SiO₂        | Plasma-enhanced chemical vapor deposition (PECVD) | Pd | [32] |
| P-Si        | SiO₂        | Dry thermal growth         | Al          | [33]       |
| P-Si        | HFO₂        | RF sputtering              | Al          | [34]       |
| n-Si        | SnO₂        | Spray coating              | Au          | [35]       |
| Semi-insulated GaAs | SiO₂ | Thermal oxidation            | Pt          | [36]       |
| Zn doped p-type InP | Al₂O₃/TiO₂ | ALD                        | Al          | [36]       |
| n-InP       | ZrO₂        | Pulse laser deposition (PLD) | Au          | [37]       |
| p-Si        | SiO₂        | Thermal oxidation          | Al          | [38]       |
| p-Si        | HFO₂        | Metal-organic chemical vapor deposition (MOCVD) | Pd | [39] |
| n-InP(100)  | WO₃         | Thermal sputtering         | Cu          | [40]       |
| n-InP       | Fe-doped ZnO | Electron beam evaporation  | Au          | [41]       |
| p-Si        | ITO, ZnO    | RF sputtering              | Au, Al      | [42]       |
| p-GaAs      | TiO₂        | DC sputter                 | AuZn alloy  | [43]       |
| n-InP       | SiO₂        | Liquid phase deposition    | In-Zn alloy | [44]       |
| n-GaAs      | HFO₂        | ALD                        | Ti          | [45]       |

Table 2. Physical Properties Comparison of Si, GaN, SiC, and β-Ga₂O₃ semiconductor. Reproduced from [4]. © IOP Publishing Ltd. All rights reserved.

| Material | Bandgap $E_g$ (eV) | Electron mobility $\mu$ (cm² V⁻¹ s⁻¹) | Breakdown electric field $E_{br}$ (MV cm⁻¹) | Baliga’s FOM $(\epsilon \mu E_{br})$ | Thermal conductivity $\lambda$ (W cm⁻¹ K⁻¹) |
|----------|--------------------|----------------------------------------|---------------------------------------------|-------------------------------------|---------------------------------------------|
| Si       | 1.1                | 1400                                   | 0.3                                         | 1                                  | 1.5                                         |
| GaN      | 3.4                | 1200                                   | 3.3                                         | 870                                | 2.1                                         |
| SiC      | 3.3                | 1000                                   | 870                                         | 340                                | 2.7                                         |
| β-Ga₂O₃ | 4.7 to 4.9         | 300                                    | 2.1                                         | 2.1                                | 0.11                                        |
| InP      | 1.35               | 700                                    | 5.10⁵                                      | 0.15                                | 0.68                                        |
| GaAs     | 1.424              | 1000                                   | 4.10⁵                                      | 0.15                                | 5.39                                        |
Chen et al [39] coproduced Pd/GaAs and Pd/InP MOS Schottky diodes as hydrogen sensors, with the cross-section of the structures. It was shown that interfacial oxide significantly improves barrier height resulting from the Fermi level pinning weakening for both GaAs and InP Schottky structures [47]. Thus, the Pd/InP MOS Schottky diode performs better and shows a large modulation in barrier height and sensitivity.

The study of radiation effects on MOS devices is important, as radiation exposure of these devices may alter the electrical and dielectric properties of the oxide layer. The radiation may cause the creation of new charge states at the SiO2/Si interface [48]. In addition, the high-energy particles can introduce lattice defects that act as recombination centers for the majority/minority charges, resulting in degradation of device performance.

Recently, Juang et al [49] fabricated an Au/SnO2/n-LTPS (n-type low-temperature polysilicon) MOS Schottky diode to prepare a glass substrate for carbon monoxide sensing applications (figure 3). SnO2 with a large bandgap of 3.0 eV is a low cost and highly sensitive material to CO gas. The experimental results show that the Schottky diode with a SnO2 layer exhibits a high relative response ratio of $\sim 546\%$ to 100 ppm CO ambient under conditions of 200 $^\circ$C and $-3$ V bias. The Schottky barrier height is given by equation (1) and the barrier height lowering ($\Delta \Phi_B$) under various CO gas concentrations is expressed as follows: [49],

$$\Delta \Phi_B = \Delta \Phi_B,_{air} - \Delta \Phi_B,_{CO}$$

Different MOS materials, such as ZnO, SnO2, WO3, and TiO2, are utilized for sensing films as they offer low costs, long lifetimes and better sensitivity and selectivity over conventional solid-state gas sensors [50]. One research study [31] involved the fabrication of a Pd/TiO2/Si MOS-based detector utilized for the detection of hydrogen and hydrocarbons, such as ethanol, acetone, and TCE in different ambient atmospheres (O2, N2, and Ar). The results show that the MOS sensor displayed a maximal response toward acetone in oxygen ambient among the other vapors detected.
2.1. Comparison between MS and MOS devices

Since the performance and stability of MS devices depend on the surface conditions, it is integral to understand its underlying mechanism. The addition of the interfacial layer and interface surface states can considerably change the device characteristics. For the ideal behavior of an MS Schottky diode approaching an ideality factor to unity, low series resistance and low reverse leakage current are required. However, the electrical properties of the MS Schottky diodes are determined by various non-idealities, such as interface states, the interfacial oxide layer, and series resistance. Direct deposition of metal on a semiconductor generates many interface states at the semiconductor surface. The higher interface state density is a cause for non-ideal current-voltage characteristic behavior. The crucial effect of adding an oxide layer on the semiconductor surface is to passivate the dangling bonds. This passivation can reduce the anomalies in the diode current-voltage characteristic behavior by minimizing the surface states [52]. Another important aspect of the oxide interfacial layer between the MS Schottky diode is to achieve a low leakage current. For high power, high frequency and high-temperature application devices, MS junctions may suffer from high leakage-current and low breakdown voltage, which limit device performance, reliability, and stability. This is where the deposition of a thin oxide/insulator layer can restrain the leakage current. Rajagopal and Venkata Prasad [53] studied the effects of a high-k ZrO2 thin insulating layer on the electrical and carrier transport properties of an Au/ZrO2/n-GaN MIS junction. The measured I-V characteristics of Au/n-GaN MS and Au/ZrO2/n-GaN MIS junctions are shown in figure 4.

Figure 4. I–V characteristics (a) and plot of Nss versus Ec–Eg (b) of Au/n-GaN and Au/ZrO2/n-GaN Schottky junctions with a schematic diagram of Au/ZrO2/n-GaN diode (inset). Reprinted from [53], Copyright (2018), with permission from Elsevier.

I–V characteristics show that the reverse leakage currents are 2.301 × 10–8 and 5.566 × 10–11 A at –1 V for the MS and MIS junctions, respectively. About a three orders of magnitude reduction in the reverse leakage current is observed for the MIS junction compared with the conventional MS junction. The results also show the increase in barrier height (0.94 eV) for MIS junction compared with the MS junction (0.73 eV) and a decrease in interface state density (Nss) figure 5 (right) for the MS junction inserted with ZrO2 is observed. Figure 5, 6 and 7 show a comparison between the energy level diagrams of Au/n-GaN and Au/ZrO2/n-GaN junctions with interface states and an interfacial layer.

2.2. Equations to MOS Schottky diode: carrier transport mechanisms

For an ideal Schottky diode, the voltage drop bias across the depletion is presented by V, whereas, in the presence of the interfacial layer, the bias voltage drop depletion is presented as V/n at semiconductor or metal interface or in the case of non-ideal Schottky diode [55]. According to the thermionic emission theory, in forward bias current voltage (I–V) characteristics when the applied bias V ≥ 3kT/q for a MOS Schottky diode is given by the following relation [56, 57].
where $n$ is the ideality, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $q$ is the electron charge, $R_S$ is the series resistance, and $I_0$ is the saturation current determined by:

$$I_0 = A A^* T^2 \exp \left( -\frac{q \Phi_{BO}}{kT} \right)$$

(3)

Where $A$ is the diode area, $A^*$ is the effective Richardson constant (32 A cm$^{-2}$ K$^{-2}$ for p-type Si), and $q \Phi_{BO}$ is the barrier height at zero bias. The ideality factor and saturation current $I_0$ can be determined using the slope and intercept of the semi-log forward bias $\ln I-V$ characteristics. The following relation gives the ideality factor ($n$),

$$n = \frac{q}{kT} \left( \frac{d(V - IR_S)}{d(\ln I)} \right)$$

(4)

For an ideal MOS Schottky diode, the value of $n$ is unity. Another model for extracting the Schottky diode characteristic parameter, $I-V$ characteristics can be used in the following function [58]:

Figure 6. Example of experimental semi-log reverse and forward bias I-V characteristics (Cetin et al [54]). Reprinted from [54], Copyright (2005), with permission from Elsevier.

Figure 7. Example of reverse bias $C^{-2}-V$ characteristics (Cetin et al [54]). Reprinted from [54], Copyright (2005), with permission from Elsevier.
\[
\frac{dV}{d(ln(I))} = n \frac{kT}{q} + R, I
\]  
(5)

\[
H(I) = V - n \frac{kT}{q} \ln\left(\frac{I}{AA^*T^2}\right) = n \Phi + R, I
\]  
(6)

Equations (4) and (5) resemble a straight-line equation. The device parameters, such as ideality factor (n), barrier height ($\Phi{b}$) and series resistance ($R_s$), can be determined from the plots $dV/d (ln I)$ versus I and $H(I)$ versus I. The Norde function also provides the diode parameters and barrier height, as defined by the following relations [59]:

\[
F(V, I) = \frac{V}{\gamma} - \frac{kT}{q} \left(\frac{I}{AA^*T^2}\right)
\]  
(7)

\[
\Phi{b} = F(V_{min}) + \frac{V_{min}}{\gamma} - \frac{kT}{q}
\]  
(8)

The reverse current, according to the Poole-Frenkel emission theory, is defined by the relation [62]:

\[
I_R = I_c \exp\left(\frac{S_{PF} V^{1/2}}{kTd^{1/2}}\right)
\]  
(10)

and the Schottky emission theory gives the following reverse current relation [60]:

\[
I_R = AA^*T^2 \exp\left(-\frac{\Phi{b}}{kT}\right) \exp\left(\frac{S_{SE} V^{1/2}}{kTd^{1/2}}\right)
\]  
(11)

where $d$ is the thickness of the film and $S_{PF}$ and $S_{SE}$ are the Poole-Frenkel and Schottky field lowering coefficients, respectively. The theoretical value of the SPFE ($\beta = 1$) is twice the value of SSE ($\beta = 2$) and can be defined as [63]:

\[
S_{PF} = 2S_{SE} = \left(\frac{q^3}{\pi \varepsilon_i \varepsilon_0}\right)^{1/2}
\]  
(12)

The non-idealities in the Schottky diode behavior occurs due to the defects at the oxide-semiconductor interface, resulting in large density of interface states that are continuously distributed within forbidden energy gap. It is a non-ideality condition, which causes leakage currents to flow. The barrier height of a Schottky diode due to the presence these interface states is strongly dependent on the electric field in the depletion region and thus it depends on the applied bias. The effective barrier $\Phi{e}$ is defined as [64]:

\[
\frac{d\varepsilon}{dV} = \beta = 1 - \frac{1}{n(V)}
\]  
(13)

\[
\varepsilon = \varepsilon_{BO} + \beta(V - IR) = \varepsilon_{BO} + \left(1 - \frac{1}{n(V)}\right)(V - IR)
\]  
(14)

Where $\beta$ is the voltage coefficient of the effective barrier height $\Phi{e}$. Hence, the effective barrier is a parameter that take cares of the effects of interface states in equilibrium with the semiconductor, as described by the theory in [65]. The ideality factor relation for a MOS Schottky diode having interface states Nss in equilibrium with semiconductor is given by:

\[
n(V) = 1 + \delta \left[\varepsilon_{s} + \frac{qN_{ss}}{W_{D}}\right]
\]  
(15)

where $\varepsilon_{s}$, $\varepsilon_{o}$, $\delta$, $W_{D}$ and $N_{ss}$ are the interfacial layer permittivity, the semiconductor permittivity, the thickness of the interfacial layer, the depletion layer width and the density of the interface states, respectively. The density of interface states (Nss) considering series resistance and voltage dependent ideality factor n(V) is given as follows [65]:
\[
N_d(V) = \frac{1}{q} \left[ \frac{\varepsilon_t}{\delta} (n(V) - 1) - \frac{\varepsilon_s}{W_0} \right]
\]  

(16)

Furthermore, the energy of the interface states \( E_{ss} \) (for p or n-type semiconductors) with respect to the bottom of the conduction or top of the valance band, at the surface of the semiconductor is given by:

\[
E_{ss} - E_V = q(\Phi_t - V) \quad (17)
\]

\[
E_{ss} - E_{cb} = q(\Phi_t - V) \quad (18)
\]

From the C-V characteristics of the MOS Schottky diode depletion layer, the capacitance per unit area can be expressed as [66]:

\[
\frac{1}{C^2} = \frac{2(V_{bi} + V)}{A^2 \varepsilon_o \varepsilon_s q N_A}
\]

(19)

\[
\frac{d (C^{-2})}{dV} = \frac{2}{A^2 \varepsilon_o \varepsilon_s q N_A}
\]

(20)

where \( A \) is the area of the diode, \( V \) is the applied voltage, \( \varepsilon_o \) is the permittivity of free space, \( \varepsilon_s \) is permittivity of semiconductor, \( q \) is the electron charge, \( V_{bi} \) is the diffusion potential at zero bias and \( N_A \) is the acceptor concentration. The value of \( V_o \) can be determined from the intercept of the \( C^{-2} \) versus \( V \) plot.

\[
V_{bi} = V_o + KT/q
\]

(21)

The barrier height \( \Phi_B \) from the C-V characteristics can be obtained by the following relation:

\[
\Phi_B (C - V) = V_{bi} + E_P - \Delta \Phi_B
\]

(22)

where \( E_P \) is the energy difference between the bulk Fermi level and is given by the following relation [65]:

\[
E_P = \frac{kT}{q} \left[ \frac{N_V}{N_A} \right]
\]

(23)

Where \( N_V \) is the effective density of the states in the valence band and is given by:

\[
N_V = 4.82 \times 10^{15} T^{3/2} \left( \frac{m_h}{m_0} \right)^{1/2}
\]

(24)

where \( m_h^* \) is the effective mass of holes and \( m_0 \) is the rest mass of electron. \( \Delta \Phi_B \) is the image force barrier lowering and is expressed by [66]:

\[
\Delta \Phi_B = \left( \frac{qE_m}{4\pi\varepsilon_o\varepsilon_s} \right)^{1/2}
\]

(25)

where \( E_m \) is the maximum electric field and is given as:

\[
E_m = \left( \frac{2qN_A V_o}{\varepsilon_s \varepsilon_t} \right)^{1/2}
\]

(26)

The voltage and frequency dependence of the C-V characteristics is due to the non-ideal behavior of a Schottky device and a series resistance effect. The series resistance for a MOS Schottky device is obtained by Nicollian and Goetzberger method [67]:

\[
R_s = \frac{G_m}{G_m^* + (\omega C_m)^2}
\]

(27)

where \( G_m \) and \( C_m \) are the measured conductance and capacitance, respectively. This series resistance effect must be adjusted to obtain the correct conductance value and capacitance. Thus, the adjusted values of capacitance and conductance are given by the following relations [66]:

\[
G_{adj} = \frac{(G_m^2 + \omega^2 C_m^2) a}{a^2 + \omega^2 C_m^2}
\]

(28)

\[
a = G_m - (G_m^2 + \omega^2 C_m^2) R_s
\]

(29)

Hill–Coleman [68] gave another method to find the density of states, which is defined as:

\[
N_d = \frac{2(G_{adj,max}/\omega)}{qA} \left( 1 - C_m/C_{ox} \right)^2 + \left( \frac{G_{adj,max}}{\omega C_{ox}} \right)^2 \right)^{-1}
\]

(30)

where \( C_{ox} \) is the oxide layer capacitance, \( \omega = 2\pi f \) is the angular frequency, \( A \) is the diode area, \( q \) is the electrical charge, \( G_{adj,max} \) is the maximum from corrected \( G_{adj} - V \) curve and \( C_m \) is the diode capacitance corresponding to \( G_{adj,max} \).
2.3. Recent progress of MOS devices and their applications

Many research efforts have been dedicated to finding a suitable insulating material for MOS/MIS Schottky diodes. In recent years, oxide semiconductors with high-k dielectrics, such as TiO₂, WO₃, MoO₃, and ZrO₂ [69, 70] have received significant attention as interface layers in SBDs. Besides the unique electrical and optical properties of oxide semiconductors, the tunability of these properties by an appropriate doping level, the ability to grow a variety of nanostructures and the number of growth methods make them superior compared to conventional silicon dioxide used in SBDs. For instance, WO₃ is an insulating layer and was employed as an intermediate layer for a metal and semiconductor in an SBD for hydrogen sensing applications [71]. Marnadu et al [40] studied the effect of strontium doping on a Cu/Sr-WO₃/p-Si Schottky diode. A thin film of strontium-doped tungsten oxide with various concentrations (0, 4, 8 and 12 wt%) was spray coated onto a p-Si substrate. It revealed that optical, morphological, and structural properties of the film change with Sr doping concentration. The XRD patterns showed a higher average crystallite size for 12 wt% Sr-WO₃. The I - V characteristics of ZrO₂ with the ALD method as a gate dielectric for metal oxide semiconductor high electron mobility transistors (MOSFETs) revealed that optical, morphological, and structural properties of the film change with Sr doping concentration. The XRD patterns showed a higher average crystallite size for 12 wt% Sr-WO₃. The I - V characteristics for SBD show the minimum ideality factor (n = 2.39) and maximum barrier height (Φ_b = 0.57 eV) values for a higher concentration (12 wt%) of Sr film.

GaN-based HEMTs are required for high frequency, high power, and low noise applications. Despite these wonderful applications, these HEMTs show a limit in their performance due to gate leakage current that limits the gate voltage swing and the maximum channel current that may be reached, which can be resolved with the addition of a dielectric layer between the gate metal and semiconductor. Ye et al [72] deposited a 10 nm thin film of ZrO₂ with the ALD method as a gate dielectric for metal oxide semiconductor high electron mobility transistors (MOSFETs). The study found that the proposed ZrO₂ AlGaN/GaN MISHEMTs have max drain current density with high transconductance and four orders of magnitude reduced gate leakage current compared to Schottky barrier HEMTs. Kim et al [73] reported a near-infrared photodetector based on a Ni/SiO₂/Si Schottky diode. The reports show that the highest performing detector showed a high rectification ratio of 19560 with an improved barrier height of 0.75 eV. The ideality factor of the photodetector was reported to be 1.14.

Hydrogen is an eco-friendly alternative fuel, which has potential to replace fossil fuels but is volatile in nature. Despite it, increased demand for hydrogen sensors is found for efficiently detecting hydrogen gas leakage. Chen et al [39] fabricated a Pd/H₂O₂/GaN MOS Schottky diode for hydrogen sensing and showed that the response time decreases from 39 to 5.3 s and 42 to 2.5 s when temperature increases from 300 to 383 K, respectively. However, it reported a lower detection limit of 5 ppm H₂ in air and showed a higher sensing response of 4.9 × 10⁵ under 1% H₂ in air gas at 300 K. In contrast, devices in comparison Pd/Al₂O₃/AlGaN [74] and Pt/SiO₂/GaN [75] showed sensing responses of 3.9 × 10⁴ and 4.5 × 10⁴, respectively, at 300 K.

Thapaswini et al [76] used a high-k Ba₀.₆Sr₀.₄TiO₃ BST interlayer to study the electrical properties of an MS Schottky diode. The atomic force microscopy images showed a smooth BST insulating thin film on an n-InP substrate. The values for n and Φ_b were calculated from I - V characteristics for the Au/n-InP MS and Au/BST/n-InP MIS Schottky diodes as 1.94 and 0.74 eV and 2.05 and 0.83 eV, respectively. The reported reverse leakage current of the Au/BST/n-InP MIS diode (5.01 × 10⁻¹⁰ A at −1 V) is lower than the Au/n-InP (2.76 × 10⁻⁹ A at −1 V) MS diode, which is a very low reverse leakage current compared to other studies. It was also found that the Poole-Frenkel emission dominates the reverse current in both diodes, indicating the presence of structural defects and trap levels in the dielectric film. The density of states values for Au/BST/n-InP with Rs was found to be 2.97 × 10¹⁷ eV⁻¹ cm⁻², which is of the same order as in [44].

Racko et al [77] have extended the Shockley-Read-Hall recombination-generation theory of trap-assisted tunneling and highlighted the current leakage that occurs in Schottky structures with a high Schottky barrier (above 1 eV) and a high traps density. It showed that in some conditions that trap-assisted tunneling (TAT) is crucial than the direct tunneling such as the charge transport is dominated by the TAT mechanism in a reverse-biased Schottky structure, whereas, direct tunneling maintains its dominance in the forward-biased structure. It emphasizes that the simulation of real Schottky diodes I - V curves need to be simultaneously considerate to thermionic emission-diffusion transport theory (TED), direct tunneling, and trap-assisted tunneling.

2.3.1. Oxide semiconductor-based thin-film electronic devices

Oxide semiconductors can provide a replacement to conventional semiconductors, such as amorphous silicon materials, transparent conducting oxides, and organic semiconductors [78, 79]. Their useful electrical and optical properties in a single material make them useful for several application fields. Oxide semiconductor thin films have huge applications in the field of electronics devices, such as flat screens, photovoltaic devices, display devices (liquid crystal displays), touch screens, gas sensors, electro-chromic devices, dilute magnetic semiconductors, ozone sensing devices, dye-sensitized solar cells and light-emitting diodes (LEDs) due to their high conductivity and good transparency [79–85].

The n-channel MOSFET exhibits good electrical characteristics with a maximum transconductance of 135 mS mm⁻¹ and electron channel mobility of 275 cm²/Vs. In another study [86], Jin et al [86] used sulphur
passivation the InP by rapid annealing the substrate under a H2S atmosphere and a MOS capacitor was fabricated with a HfO2 film using ALD. The report shows the electrical properties of the device were improved. A serious issue with the III–V MOSFETs is the high defect density between the III–V material and the high-k dielectric layers. Therefore, the solution to this problem is to create a shallow InGaAs buried channel with an InP barrier layer, which moves the channel away from the oxide material and mitigates the problem of high density of states at the high-k/InP interface. Another study by Ahmadi et al [87] highlighted the passivation of the surfaces as well as the Fermi level depinning with the use of hydrogen and H-sensors. The measurement in the study revealed that the Schottky barrier height can possess similar values for the varied β-(AlxGa1−x)2O3 composition. It stated that this might be due to changes in alloy’s composition.

Although, these buried channel techniques work, a significant defect density at the barrier layer and channel interface still exist, which affect the subthreshold swing and threshold voltage [88]. Zhuo et al [89] studied the electrical properties of the Al2O3/InP interface of a MOS capacitor and showed that an interface with reduced positively charge defects was achieved.

Zhang et al [90] reported Co-doped SnO2 thin films and explored their hydrogen gas sensing properties. The results indicate that the best performance was obtained for a 1 mol% Co-doped SnO2 thin film at 225 °C with a response time of 7 s at 2000 ppm H2 gas pressure. The researchers in [89] fabricated Al-doped ZnO (AZO) thin films by DC sputtering to study the electrical characteristics of an AZO/p-Si heterojunction. The rectify ratio at 5 V was found to be as high as 19.7. The results show that the diode can be used as a photodetector. Park and Kim [91] demonstrated a transparent photodetector based on a TiO2 film. Li and N co-doped ZnO films were produced by a molecular epitaxy technique, and their electrical properties were studied in [92]. The film was used in fabricating a photodetector. The photodetector showed an excellent response even for very weak signals with a power density as low as 20 nW. The report states that the high performance of the photodetector could be attributed to the relatively low carrier concentration of the ZnO:(Li, N) films caused by the compensation of the incorporated acceptors to the residual donors. Van Meirhaeghe et al [93] study showed that the for GaAs and InP Schottky’s barrier height can be increased through deposition technique.

2.3.2. N-type metal oxide semiconductors

Both n- and p-type thin-film oxide semiconductors are required for various optoelectronic applications. Doping is a tool for controlling the properties of these oxide thin films. Ga2O3, SnO2, In2O3, CdO and ZnO are widely known n-type semiconductor oxides [94]. Zinc oxide-based metal oxide semiconductors have been investigated extensively due to their various applications such as a diode, sensors, and solar cells in recent years. Zinc oxide is a promising material for electronic devices due to its optical bandgap and electrical conductivity. This material is a direct bandgap with n-type electrical conductivity. There are several studies on ZnO thin film properties with IIIA (In, Al and Ga) metals and transition (Cu, Co, Ni, Mn, Ti, and Cd) metals doped, to enhance the electrical and optical properties of ZnO thin films [95, 96].

2.3.3. P-type metal oxide semiconductors

In contrast, transparent p-type conductors have been less explored but are becoming more popular recently. The conductivity values for p-type materials are less compared to n-type materials for the same transparency because of the lower mobility values for p-type carriers [97]. A NiO thin film with a bandgap of 3.6–4.0 eV was employed to fabricate an Au/NiO/MgZnO/In structured MIS photodetector [98]. The results show that inserting the NiO not only lowered the dark current but also enhanced the photo response of the photodetector. Fortunato et al [99] also reported p-type conductivity in a CuO2 thin film. The workers also reported a thin-film transistor based on a CuO2 thin film, showing improved electrical performance in this research. Singh et al [100] obtained p-type ZnO thin films by bismuth (Bi) doping using a sol-gel method. The p-type nature of the Bi-doped ZnO thin film was confirmed by Hall measurements and a hot point probe method. Finally, a Pd/Bi-doped p-type ZnO Schottky diode was fabricated successfully. Several methods have been reported to prepare high-quality oxide semiconductor thin films in the literature, such as pulsed-laser deposition, MOCVD, molecular beam epitaxy, magnetron sputtering, electron beam evaporation, spray pyrolysis, vacuum evaporation, chemical deposition, ALD, successive ionic layer adsorption and reaction, electrochemical techniques and sol-gel spin coating methods.

2.3.4. Electrical and optical properties of oxide semiconductors

Davoodi et al [101] studied the effect of Ti and Al co-doping on the electrical and optical properties of ZnO thin films. They found that with the increase in Ti content doping level into the ZnO thin films, the crystal size decreases from 23 to 15 nm, and the surface roughness decreases. Yilmaz [102] investigated the properties of ZnO:Ga thin films because Ga3+ is considered as an efficient dopant due to its advantages in being less reactive and more resistant to oxidation compared to Al3+. In addition, with its lower diffusivity, it is less affected by diffusion problems. Jung et al [103] also reported the electrical and optical properties of Ga-doped ZnO thin
films. The films show an average transmittance above 90% in the 550 nm wavelength region. Highly c axis-oriented films with the lowest resistivity of $1.46 \times 10^{-3} \, \Omega \, \text{cm}$ were achieved.

 Mimouni et al studied the electrical and dielectric behaviors of Mn-doped ZnO films with a spray method [104]. They found that a redshift in the bandgap of the ZnO films occurs due to the substitution of Mn$^{2+}$ in the acceptor level, which causes bandgap narrowing. Giri and Chakrabarti [105] studied the structural and optical properties of Mg-doped (0–5 at%) ZnO thin films using an RF sputtering method. The optical bandgap was initially found to increase from 3.02 to 3.74 eV by increasing the Mg content from 0 to 3 at% but further increasing the Mg content decreases the bandgap to 3.43 eV for a concentration of 5 at%. The XRD results show that the maximum crystallite size of 21.73 nm was calculated for the 3% Mg-ZnO thin film and structural parameters degrade after 3% Mg doping in ZnO. It was shown that the Mg (3 at%) doped ZnO thin film could be employed as a buffer layer in optoelectronic device applications.

 Karabulut et al [17] study paired the Au/Ti/HfO$_2$/n-GaAs Schottky structures with the use of magnetron dc sputter technique. It showed the dependence of the temperature of the electrical and dielectric properites, which was obtained using the G/ω–V dates and C–V. It also showed that the dielectric values ($\varepsilon'$, $\varepsilon''$, tanδ and $\sigma_{ac}$) decreases at high temperature.

 Çetinkaya, Sevgili, and Altundal [106] assessed the effects of the Al/p-Si (MS) type photodiodes interlayer fabrication using (92 ZnO-doped CuO) for its electrical properties. It used an I-V (reversed and bias) measurements for dark and other illumination intensities (10–100 mW cm$^{-2}$). The results showed that values increase with the illumination intensity, particularly for the reverse bias because of high electric field. Altundal et al [107] study fabricated the Au/Ag-doped ZnO/polyvinyl pyrrolidone (PVP)/n–Si SBDs. X-ray diffraction and SEM results showed that small nanocrystals formation. While the formation of ZnO nanostructures was sheet like.

 Among III–V compound semiconductors, InP is an attractive material for optoelectronic and high-frequency applications but has a major issue of leakage current. This issue can be resolved by adding an insulating layer between the MS junction and reduce the effective barrier height. For comparison purposes, various parameters extracted from the I–V and C–V characteristics of the Au/n-InP MS and Au/ZrO$_2$/n-InP MIS diode are given in table 3. The results show that intermediate oxide layer plays an important role and effectively reduced the leakage current in the Au/n-InP Schottky diode.

 The primary challenges are observed in electronic system such as material challenges, material diffusion, intermetallic formation, along with temperature-gradient-induced mechanical stress. Consequently, some challenges emerge at device level such as contacts with high performance, dielectrics, interconnects, controlled doping, encapsulation materials, complementary field-effect-transistors as well as robust imperfections. The problem or opportunity is to use semiconductors for producing extreme-environment sensors that can co-located power as well as process data. Accordingly, material development along with device optimization are required for Schottky diodes to operate at an extremely high voltage. This can be done with integration of alloys in the unipolar devices that have high Al composition.

 Extensive research activities have focused on the development of various high sensitivity capable gas sensors for industrial and environmental applications. There is a huge demand for highly sensitive gas sensors for various industrial and environmental applications. Hydrogen sensors are one such example, which is used in industry, medical treatment, and hydrogen-fueled vehicles, where the detection of hydrogen gas leakage is required.

### Table 3. Comparison of various parameters determined from the I–V and C–V characteristics of Au/n-InP MS and Au/ZrO$_2$/n-InP MIS diodes. Reprinted from [37], Copyright (2016), with permission from Elsevier.

| Sample                      | MS diode | MIS diode |
|-----------------------------|----------|-----------|
| Barrier height $\Phi_B$ (eV) from I–V | 0.59     | 0.69      |
| Ideality factor (n) from I–V | 1.39     | 1.99      |
| (n) from $dV/d(lnI)$         | 1.42     | 2.09      |
| $\Phi_B$ (eV) from H(I)      | 0.63     | 0.72      |
| Series resistance $R_s$ (KΩ) from $dV/d(lnI)$ | 121.68   | 155.47    |
| $R_s$ (KΩ) from H(I)         | 125.26   | 168.17    |
| $\Phi_B$ (eV) from C–V      | 0.85     | 0.97      |
| Interface state density $N_{ss} \times 10^{12}$ (eV$^{-1}$ cm$^{-3}$) from I–V and C–V | 13.90–3.72 | 3.06–1.17 |
2.4. Future directions
With the continuous growth of electronic consumer products, there is an increasing demand for high performance and reliable electronic devices, including MOSFETs, solar cells, photovoltaic devices, gas sensors, photodetectors, display devices, and LEDs. Therefore, there is still a need to develop an efficient and near-ideal diode for these essential applications. Continuous research on this topic will lead to new paths and discoveries. Nanostructures, owing to their interesting properties and higher surface to volume ratio, have attracted the attention of many researchers. As reported in thin-film nanostructures [41, 108], they can be used effectively as interfacial layers in MOS Schottky diodes. The grains and grain boundaries at the interface can significantly affect the Schottky diode properties. One-dimensional nanorods or nanowires can be employed efficiently for gas detection. Further doping of these nanostructures can increase the surface to volume ratio and hence better sensing properties can be obtained by fabricating nanostructured diode-based detectors.

High-k dielectrics may have the potential to replace conventional SiO$_2$. High-k dielectrics offer enhanced capacitance, high-energy storage, high breakdown voltage, and low leakage current. Some reports have been reviewed in this article for their use in MOS Schottky diode applications. Metal oxides, hybrid and organic polymer-based materials or graphene may also be used as future materials for Schottky diode applications. In recent years, conjugated conducting polymers have become popular for optoelectronic applications. Several research reports have focused on modifying the optical and electrical properties of polymers by doping with transition metals, such as Zn, Co, Ni, Cu, and Fe [108–110]. Investigations and research are being carried on metal-doped polymer-based Schottky barrier diodes to develop low leakage and electrically superior diodes. Polyyvinyl alcohol (PVA) with high dielectric strength (>1000 kV mm$^{-1}$) is potentially an attractive candidate to study as an organic intermediate layer in Schottky barrier diodes. For example, [108] reports the fabrication of PVA doped with Ni, Zn nanofiber film on a silicon substrate using an electrospinning technique as an intermediate layer for an MS diode.

Mousavi et al [111] explored ZnO with graphene quantum dot core–shell structures induced as filler into a PVA matrix for optoelectronic applications. Yuksel et al [112] studied perylene-monoimide as an interlayer in an Au/p-Si Schottky diode. There is a wide variety of polymers available, which are investigated as interfacial layers in Schottky diodes [113–115], and this area of composite polymers still demands greater research focus. Graphene oxide can be doped with different elements (e.g., B, N, S, and Si) to control its electrical properties [116]. This makes it a favorable material for several applications, such as transistors, diodes, supercapacitors, and batteries. Studies have shown the use of graphene and a graphene oxide-doped NiO nanocomposite as an interfacial layer in Schottky diodes [117, 118]. Little attention has been given to transition metal oxides (TMOs), and there are few reports of TMO-based MOS Schottky diodes [119], with no significant reports found on TMO/polymer hybrid composite based Schottky diodes. To fully exploit the potential of these materials, there is a need for further research and investigations.

Nanostructured graphene material is one of the suitable candidates for an appropriate metal barrier that might help improve the limit of junction temperature as it has metallic behavior with outstanding electronic and thermal properties [119]. A graphene nanowall as a Schottky barrier material was used on a trench MOS barrier Schottky diode. It was grown by plasma enhanced chemical vapor deposition, using n-type epitaxial silicon wafer as a substrate. This material gives an excellent result in the performance of high-temperature leakage current [119]. This gives a high breakdown voltage and is capable of handle much higher temperatures without thermal runaway for the examined device.

3. Conclusion
The knowledge obtained through research on semiconductor junctions has opened doors for several new inventions and devices. It helps to develop a better understanding of MOS and MS devices, which has led to new and better technology products. MS Schottky diodes, which may be considered as core devices and are one of the earliest solid-state devices invented, has several applications. MS Schottky diodes suffer from poor electrical performance due to strong Fermi-level pinning and metal induced gap states present at the interface. Adding an interfacial oxide layer plays a significant role in determining the electrical properties of the Schottky diode. The interfacial oxide layer in high frequency and high-power devices can effectively reduce the leakage current, but on the other hand, it may have drawbacks such as the lack of stability and drift effects. This detailed study demonstrated that metal oxide/insulator semiconductor Schottky devices are characteristically dominated by the intermediate layer and interface properties. Since the ultimate device reliability and performance is intimately related to the surface conditions, understanding and investigating the device surface physics is very important in a MOS Schottky diode.
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