Review of GaN Nanowires Based Sensors

Ahmed M. Nahhas*
Department of Electrical Engineering, Faculty of Engineering and Islamic Architecture,
Umm Al Qura University, Makkah, Saudi Arabia
*Corresponding author: amnahhas@uqu.edu.sa
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Abstract This paper presents a review of the recent advances of GaN based nanowires sensors. GaN has gained substantial interest in the research area of wide band gap semiconductors due to its unique electrical, optical and structural properties. GaN nanostructured material exhibits many advantages for nanodevices due to its higher surface-to-volume ratio as compared to thin films. GaN nanostructured material has the ability to absorb ultraviolet (UV) radiation and useful in many optical applications. Recently, GaN nanostructured based devices have gained much attention due to their various potential applications specially in nanowires sensors. GaN nanowires sensors have been used in many devices such as gas sensors, biosensors, and pressure sensors. The recent aspects of GaN based nanowires sensors are presented and discussed. The performance of several sensors based devices which have been demonstrated on GaN is reviewed. The structural, electrical, and optical properties are also reviewed.

Keywords: gallium nitride (GaN), nanostructured, doping, nanowires, sensors, ultraviolet (UV)

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1. Introduction

The group III-Nitride semiconductor materials have attracted a lot of interest for new generation of optoelectronic devices [1]. The advantage with these materials is the flexible bandgap varying from 0.7 to 6 eV hence covering an ultra-broad spectrum, from deep ultraviolet up to near infrared [2], allowing the development of numerous applications. Solar cells based on nitride materials have readily been investigated for terrestrial and space-based applications [3]. Transistors performance for high power electronics, ground-based communications and biological agent detection devices has been enhanced [4]. Major efforts have been dedicated to the technological fabrication in order to achieve efficient emitters and detectors [5]. Recent progress has demonstrated cutting edge results in high-speed data rate connectivity and integrated circuits [6]. Imaging sensors on high speed electronics have been implemented founded on their sensitive applications in security screening [7].

GaN as a member of group III-nitride family has become the revolutionary material owing to its electronic and optical properties. The direct, flexible and wide bandgap makes GaN material a key candidate for achieving high frequency, large bandwidth, high power and efficiency devices. GaN based detectors are in particular suitable for full color display, high density information storage, and UV communication links [8].

GaN is a very hard, chemically and mechanically stable wide bandgap (3.4 eV) semiconductor material with high heat capacity and thermal conductivity which makes it suitable to be used for sensors [9], for high power electronic devices such as field effect transistor (FET) [10] and for optoelectronic devices such as light emitting diode (LED) [11]. The optical properties of GaN nanostructured are of great current interest because of the potential application in solid state lighting [12]. In n-type GaN, an UV peak at approximately 3.42 eV usually dominates the photoluminescence spectrum [13].

2. GaN Nanostructured Materials

Doping

GaN nanostructured material exhibits many advantages for nanodevices because of its higher surface-to-volume ratio as compared to thin films. The GaN nanostructured material has ability to absorb UV radiation and immense in many optical applications [17]. GaN nanostructured have various shapes including nanowires [18], nanoparticles [19], nanobelts [20], nanorings [21], nanotubes [22], nanodots [23], and nanorods [24]. GaN nanoparticles generated lot of interest
among scientists as well as technologists during past few years. The electronic properties of quantum confinement of electrons of nanoparticles make them very useful in electronic industry including many GaN applications [25].

GaN doping is very important for different devices structures. Several techniques have been used in GaN doping. The ion implantation technique for controlling n-type or p-type conduction has been a significant challenge for GaN based high-power devices to achieve levels approaching their theoretical limits of performance [26]. Previous studies on n-type conduction of GaN through silicon ion implantation achieved 86% [27], and approximately 100% [28] of activation rate after annealing at 1250 and 1400°C, respectively. Such high temperature annealing results in serious surface degradation of GaN due to decomposition [29], thereby needs a protective layer. However, it is difficult to make a proper choice of a protective layer which remains unaltered and is removable after annealing above 1200°C. Therefore, achieving the high activation rate at lower temperature is a very important practice. On the other hand, the magnesium (Mg) ion implantation for p-type conductivity is more challenging due to the higher temperature annealing required for electrical activation, resulting in a major difficulty protecting the surface [30]. The formation energy of Mg on the Ga site (MgGa) near the valence band is about 1 eV higher than that of SiGa at the Fermi level near the conduction band [31], which may explain the difference of required annealing temperature for different conduction types. The efficient p-type doping of GaN is in general a challenging task [32]. Despite the achievements in realization of good quality p-type GaN, the activation efficiency of Mg atoms is still as low as few percent. The p-type doping of GaN is typically performed during growth, while the reports on other doping techniques common in semiconductor processing such as ion implantation [33], and diffusion [34] have been scarce. The thermal stability and redistribution of the implanted dopants in GaN revealed that implanted Mg have shown a change in the concentration profile after annealing temperatures. Indeed, post implantation annealing of GaN at high temperatures, typically 1100-1400°C, is necessary both for Mg redistribution and activation as well as lattice recovery. However, annealing above 800-900°C induces severe damages at the GaN surface due to nitrogen desorption. Because of this high sensitivity to post implantation thermal treatments, protecting the GaN surface using a cap layer is mandatory to prevent the nitrogen desorption [35,36]. Recently, GaN was also doped with carbon [37]. The Intentional doping of carbon on GaN can be done using a hydrocarbon precursor technique [38]. The extrinsic carbon doping delivers better dynamic properties for the device voltage capabilities. In some devices like GaN on silicon (Si) devices [39,40] offer an optimal solution for efficient dc-de conversion. Handling high voltage operation at high switching frequency, also have long shown clear advantage over their Si counterparts [41]. Due to the need of high blocking voltage, carbon compensation doping is the most commonly used method for achieving highly resistive GaN buffers. However, the heterostructure field effect transistors grown using carbon doped GaN suffer from serious setbacks, such as high dynamic on-resistance and slowly recovering current collapse [42]. Carbon doping has been traditionally achieved through incorporation of carbon originating from the metal organic precursor during the growth process [43,44] in a so called auto doping technique. To achieve high carbon concentrations, growth temperature, pressure, and V/III ratio had to be substantially decreased. This entailed inferior crystal quality leading to a higher dislocation density yielding lower blocking voltages and electron mobility in the channel [45]. Lately, extrinsic carbon doping of GaN buffers has been gathering momentum as a method to incorporate carbon whilst maintaining growth parameters optimized for crystal quality. GaN can also be doped with europium (Eu). It is an attractive alternative to InGaGaN for the red light LED, as the InN rich alloy has disappointingly low luminescence efficiency [46,47]. The active lumophore in the first successful GaN:Eu injection device [48] is the primary defect, Eu²⁺, an isolated Eu ion located on a Ga site, EuGa [49,50]. Association of EuGa with other defects produces a variety of centers; competition for excitation among the various rare earth related defects gives rise to ‘site multiplicity’ in solid state rare earth luminescence spectra [51]. Like wide-gap II-VI semiconductors, GaN exhibits self-compensation, so neutralization of acceptor doping by native donors, which is energetically favorable for the crystal. There is a clear experimental evidence that GaN:Mg (Zn) films and crystals have high resistivity or are n-type owing to the compensation of acceptor impurities by native defects or unintentional H and O impurities [52,53]. The thermodynamic analysis of the defect chemistry in GaN:Mg crystals [54] suggests that, under equilibrium growth conditions, a MgGa acceptor controlled p-type can only be achieved at nitrogen (N₂) pressures above 10⁵ MPa, in agreement with experimental data [55]. Magnesium is the only dopant capable of ensuring stable, reproducible p-type conduction in GaN [56]. Magnesium incorporation is accompanied by the formation of considerable amounts of intrinsic and extrinsic defects. Clearly, the incorporation of such centers has a significant effect on the electrical and luminescent properties of GaN:Mg [57]. Low temperature photoluminescence spectra of Mg-doped GaN films show broad emission bands in the range 2.8-3.3 eV, due to donor recombination [58,59]. GaN can also be doped with manganese (Mn). The growth of homogeneously Mn-doped Ga_xMn_xN thin films have been carried out at different temperatures [60]. A high dopant concentration and high carrier concentration are inherent advantages of that doping. The Mn has low solubility in gallium and its group V compounds. That phase separation occurs in the growth of GaMnAs when concentrations of over 5% Mn and temperatures of a few hundred Celsius were used during the growth process [61]. This proved an obstacle to obtaining the required magnetic semiconductor film properties for device fabrication [61]. The Pulsed laser deposition (PLD) can be used to prepare thin films from multicomponent targets and allows Mn concentrations in the GaN films to be controlled easily by varying the quantity of Mn included in the initial target preparation [62]. The growth conditions can be far from equilibrium, which offers the possibility
of reaching higher Mn concentrations without phase separation [62].

3. GaN Nanowires Sensors Based Devices

GaN nanowires have garnered much attention in recent years due to their attractive optical and electrical properties. GaN nanowires have been studied extensively [63]. GaN nanowires have been used as building units to construct different nano devices, such as nanolasers, detectors, and sensors [64]. GaN nanostructured nanowires based devices have been used extensively as a new energy efficient and environment friendly for their promising applications in gas sensing, displays, backlight units, laser diodes, traffic lights, and solid state lightening. GaN gas sensors have a greater efficiency, long life span, high reliability, and many environmental benefits [65,66,67]. Recently, GaN gas sensors have a great potential in such as hydrogen (H2), hydrogen sulfide (H2S), and nitride oxide (NO), and carbon monoxide (CO) and biochemical sensors [67,68,69,70,71]. Moreover, GaN nanowires lasers are attracting increasing research interest for ultra small coherent light sources [72]. GaN nanowires lasers are becoming key elements in a wide range of future applications, such as solid state lighting, spectroscopy, and on chip transmitters [73,74]. The lasing properties of GaN nanomaterials are very important for making useful practical applications. On the other hand, H2 gas has attracted significant attention as renewable, sustainable, and clean energy source to replace petroleum fossils. The H2 gas sensors based on GaN nanowires devices have been widely applied in many fields, such as industrial processes, space, fuel cells, and biomedical installations [75]. Over recent years, numerous GaN-based H2 sensors have been studied and reported. Among these sensors, GaN based Schottky diodes exhibit a number of advantages, including excellent sensing performance, fast response, a wide range of operating temperatures, and chemical stability due to their inherent characteristics, including a wide band gap and high exciton binding energy [75].

The AlGaN/GaN pressure sensor with a specially designed Wheatstone bridge structure was investigated and reported by Tan et al. [76]. In that study, four gateless AlGaN/GaN HEMTs were placed in pairs at the tensile stress area (near to the edge) and compressive stress area (in the Centre) of the circular diaphragm [76,77]. The study showed that the opposed stress response of the two pairs of the bridge resistances resulting in a high sensitivity of 72 μV/kPa/V for the fabricated sensor [76]. The study results showed that the device also had a large output capability of 64.8 mV/V [76]. The results of that study also showed a great potential of AlGaN/GaN devices for pressure sensing applications [76]. Figure 1 shows the schematic of the AlGaN/GaN heterostructure sensor. Figure 2 shows the output voltages as a function of pressure.

The low operating temperature nitric oxide (NO) gas sensors based on hydrogen peroxide treated GaN nanorods was investigated and reported by Reddeppa et al. [78]. In that study, a hydrogen peroxide (H2O2) treatment was used to enhance the active sites on the surface of GaN nanorods for NO gas detection [78]. In that study, the surface treatment was carried out by immersing the GaN nanorods into H2O2 solution at different temperatures for 10 min [78]. The resulted film was examined by X-ray diffraction (XRD) and photoelectron spectroscopy (XPS) to find the physicochemical properties of the GaN nanorods [78]. The XPS results of the study revealed that the active sites (O2 species) on GaN nanorods were increased by H2O2 treatment [78]. The study results showed that the NO gas sensing measurements revealed that response of the H2O2 treated GaN nanorods enhanced by 4-times than that of pristine GaN nanorods to 100 ppm of NO gas concentration at 50 C [78]. The results also showed that the H2O2 treated GaN nanorods exhibited high response under UV illuminations [78]. Figure 3 shows the FESEM images of GaN nanorods. Figure 4 shows the I-V characteristics of GaN sensor. Figure 5 shows the dynamic NO sensing properties (20-100 ppm) of GaN nanorods sensor. Figure 6 shows the responsivity of the GaN sensors. Figure 7 shows the NO gas response versus time curves as function of temperature.
The fabrication of the catalyst-free low temperature operating CO sensors using nanostructured GaN and AlGaN/GaN heterostructures based gas sensors was investigated and reported by Mishra et al. [79]. In that study, the morphological, electronic and electrical properties of the devices were thoroughly investigated [79]. The study showed that the CO sensing on GaN and AlGaN/GaN heterostructure was governed by the chemical nature of ambient-oxidation induced amorphous oxide layer, which acted as donor/acceptor state at the surface [79]. The study also showed that the critical device parameters including the Schottky barrier height and the electron accumulation associated with the series resistance and leakage current displayed significant variation with temperature [79]. The study results showed that the catalyst free CO sensing measurements divulged a sensitivity of 33% along with a response and recovery time of 94 and 44 sec at 100 °C [79]. The study also showed that the morphological analysis revealed that nanostructured surfaces pursuing lower barrier height, electron accumulation and higher amount of surface native oxide enhances CO adsorption and yield optimum sensing efficiency [79]. Moreover, the hydroxyl species associated with water vapors act as an electron donor and hence reduce the resistance leaving an adverse effect on CO sensing [79]. Figure 8 shows the FESEM images of the gas sensors. Figure 9 shows the schematic diagram representing sensing mechanism at GaN surface. Figure 10 show the change in resistance (ΔR) observed due to CO sensing (100 ppm) at different temperatures.
The GaN-high electron mobility transistor (HEMT) based sensor was investigated and reported by Chaturvedi et al. [80] for polar liquid sensing. The fabricated HEMT sensor chip was packaged by using low temperature co-fired ceramic technique [80]. The result of the study showed that the sensor had a typical drain current of 21.2 mA at 3.3 V [80]. The results also showed that the fabricated sensor had a percentage change of 1.78%, 2.18% and 6.3% in drain current for mercury chloride, copper chloride and sodium chloride respectively with respect to the drain current of pure water [80]. Finally, the study showed that the sensor was sensitive to the concentration of polar liquids so it could be used to detect the leakage or mixing of foreign substance into the liquid [80]. Figure 11 show the GaN HEMT structure. Figure 12 show the GaN HEMT sensor gate area, chip and package. Figure 13 show the response of HEMT sensor to different polar liquids.

The low electroless plating (EP)-Pd/GaOx/GaN Schottky diode-type H$_2$ sensor was investigated and reported by Liu et al. [81]. In that study, the GaOx dielectric was formed by a proper H$_2$O$_2$ treatment on the GaN surface [81]. Moreover, the EP approach of the Pd catalytic layer were employed to facilitate a high-performance metal-semiconductor Schottky contact [81]. In that study, an extremely high H$_2$ sensing response of 5.5×10$^6$ (under 1% H$_2$/air gas) and a relatively low detection limit of 5 ppb H$_2$/air are obtained at 300 K [81]. The study results showed that the corresponding response and recovery times are 22 sec and 21 sec at 300 K [81]. The study results showed that the data transmission volume could be reduced by 90% [81].
Finally, that study fabricated device is promising for the high-performance H₂ sensing and Internet of Things (IoT) applications [81]. Figure 14 shows the cross section diagram of the GaN sensor [81]. Figure 15 shows the SEM images of the GaN sensor. Figure 16 shows the schematic energy band diagram of the GaN sensor. Figure 17 shows the transient responses of the studied device at 300 K. Figure 18 shows the response and the recovery time constants of the GaN sensor. Figure 19 shows the schematic diagram showing the sensing transmission structure of the GaN sensor for IoT applications.

Figure 14. Cross section diagram of the GaN sensor [81]

Figure 15. SEM images of the GaN sensor [81]

Figure 16. Schematic energy band diagram of the GaN sensor in air and under H₂ gas ambience [81]

Figure 17. Transient responses of the GaN sensor at 300 K. The corresponding responses under 5 and 100 ppm H₂/air gases are shown in the insets [81]

The fabrication of the ZnO nanorods-GaN H₂S sensors was investigated and reported by Wang et al. [75]. In that study, the ZnO nanorods were grown on the GaN substrates by electrodeposition [75,82]. The resulted crystalline structure was investigated by HRTEM and XRD analyses [75]. The XRD results showed that the single crystal ZnO with an average size of 240 nm were grown along the c-axis direction [75]. The study results showed that the resulting sensors displayed an excellent selectivity and response [75]. The result of that study showed that the sensors exhibited high sensitivity and excellent selectivity due to the structure of ZnO and the characteristic of heterojunction [75]. The sensor also showed a sensing response time of 82 sec and a recovery time as low as 48 sec [75]. In addition, the study results showed that the results demonstrate that ZnO-GaN based gas sensor was good candidates for applications in environment H₂S monitoring. Figure 20 shows the schematic illustration of electrodeposition of ZnO-GaN gas sensors. Figure 21 shows the SEM images, TEM image, and the Photoluminescence spectra of pristine the ZnO and ZnO-GaN gas sensor.
The fabrication and characterization of the metal oxide functionalized GaN nanowire on Si substrate using production standard stepper lithography for SO₂ gas detection was investigated and reported by Khan et al. [82]. In that work, the GaN nanowires were formed on Si substrate using production standard stepper lithography and top-down approach [82]. In that study, three different functionalized devices were prepared by the deposition of metal oxides- ZnO, WO₃ and SnO₂ by optimized RF sputtering on nanowires followed by rapid thermal annealing [82]. The resulted film, crystallinity and surface topography of metal-oxide/GaN nanowires were characterized by EDS, XRD, AFM and SEM [82]. The study results showed that the ZnO-GaN sensor was found to be the best candidate for precise SO₂ detection [82]. The study results showed that the sensing properties of ZnO-GaN device such as- adsorption and desorption rate, cross-sensitivity to interfering gases, and long-term stability at extreme environmental conditions were investigated to confirm its implementation in field conditions [82]. Finally, the results indicated that ZnO-GaN sensor is a promising candidate for high performance SO₂ sensing in real-world applications [82]. Figure 22 shows the schematic process flow for the proposed GaN sensor fabrication. Figure 23 shows the EDS spectra of the fabricated GaN/AlGaN nanowire on Si substrate, XRD. Figure 24 shows the 2D AFM images of the annealed ZnO on sapphire substrate. Figure 25 shows the FESEM image of the developed bare GaN nanowire. Figure 26 shows the response fitting lines of the ZnO/GaN device.
Figure 26. Response fitting lines of the ZnO/GaN device (black), WO3/GaN device (green) and SnO2/GaN device (red) for varying concentrations SO2 gas in dry air under UV light at RT [82]

The Normally off AlGaN/GaN ion-sensitive field effect transistors realized by photoelectrochemical method for pH sensor application low operating temperature NO gas sensors based H2 peroxide treated GaN nanorods was investigated and reported by Li et al. [76,83]. In that study, the photoelectrochemical reaction transforms the AlGaN barrier into oxide, which could deplete the two dimensional electron gas to achieve the normally-off operation [83]. The study results showed that the oxide on the surface enhanced the sensitivity to approximately 56.3 mV/pH [83]. Moreover, the study results showed that the surface characterization results, the needle-like native oxide (a mixture of Al2O3 and Ga2O3) was transformed into a smooth Al2O3-dominated film [83]. Finally, the study showed that enhanced surface status and transconductance of the normally-off device is regarded as the possible reason to effectively improve the pH sensitivity [83]. Figure 27 shows the cross-section view of normally-off AlGaN/GaN ISFETs with oxide layer in the open-gate area. Figure 28 shows the RT output properties of the ISFETs. Figure 29 shows the XPS spectra of GaN sensors.

Figure 27. Schematic normally-off AlGaN/GaN ISFETs with oxide layer in the open-gate area [83]

Figure 28. RT output properties of the ISFETs (a) and MOS-ISFETs (b) measured in solutions at different reference-voltages [83]

Figure 29. XPS spectra of Ga3d, Al2p and O1s for the ISFETs without any treatment [83]

The enhancing sensitivity of the reference electrode free AlGaN/GaN HEMT based pH sensors by controlling the threshold voltage was investigated and reported by Xue et al. [84]. In that study, the threshold voltage (V_T) of the AlGaN/GaN HEMT based pH sensor was adjusted by the method of the photoelectrochemical (PEC) oxidation on the GaN cap layer surface [84]. The study showed that the PEC oxidation treatments, the V_T of the device shifted from -3.46 V to -1.15 V and the gate voltage (V_G) corresponding to the maximum transconductance (gMAX) position (V_G|gMAX) of the device shifted from -2.6 V to -0.1 V [84]. The study results showed that the drain current (I_D) variation per pH of the AlGaN/GaN HEMT based pH sensor without reference electrode increased from 0.7 μA to 14 μA when the drain voltage (V_D) was 0.5 V [84]. The study also showed that the sensitivity of the reference electrode free AlGaN/GaN HEMT based pH sensor could be significantly increased by regulating the V_T to make V_G|gMAX approached the equivalent V_G when liquid droplet on the sensing window surface (VG-EQU) [84]. The designed sensor would be useful to the miniaturization and integration of the AlGaN/GaN HEMT based sensors [84]. Figure 30 shows the schematic diagram of the GaN sensor. Figure 31 shows the measurement signals at different pH and the analysis of the V_T and gMAX of the device before the PEC oxidation. Figure 32 shows the energy band diagram of the sensor untreated by PEC.
The study of the GaN Schottky diode based H₂ sensor with a H₂ peroxide oxidation approach and platinum catalytic metal was investigated and reported by Liu et al. [85]. In that study, the platinum (Pt) catalytic metal and a H₂ peroxide oxidation approach were utilized to fabricate the H₂ sensor based on a GaN Schottky diode [85]. The study showed that the presence of a gallium oxide dielectric layer between the Pt metal and the GaN surface could increase the adsorption sites for dissociated H₂ species, thereby improving the related sensing ability towards H₂ gas [85]. The study results showed that the GaN sensor had a high sensing response ratio [85]. The study showed that the sensor exhibited a good high temperature durability and a high sensing speed [85]. The study results showed that the sensor had a high temperature durability [85]. Finally, the study showed that the Schottky diode device not only is promising for H₂ gas detection, but also could be utilized effectively in the transmission of sensing data [85]. Figure 33 shows the fabrication of the Pt/GaOx/GaN-based Schottky diode sensor. Figure 34 shows the I-V characteristics of the sensor under different concentrations of H₂ gas. Figure 35 shows the Sensing response of the GaN sensor. Figure 36 shows the transient responses of the GaN sensor.
The flower-like ZnO (FZnO) was synthesized on the GaN by electrodeposition as sensing materials of ethanol gas sensor was investigated and reported by Wang et al. [86, 87]. The designed FZnO consisting of ZnO nanosheets with thickness of 55 nm is in situ grown on GaN [86]. In that study, the FZnO-GaN heterojunction was used as sensing materials for detection of ethanol, this material possesses a higher response than ZnO or ZnO composite at RT [86]. The study results showed that the FZnO-GaN based gas sensor had sensitivity (\(R_a/R_g=26.9\)), when the sensor is exposed to ethanol at the concentration of 50 ppm at RT [86]. Moreover, the study showed that the designed sensor presents excellent selectivity and stability. In addition, the detection limit of the sensor is 100 ppb [86]. The study also showed that the enhancement of the sensing response was mainly attributed to the FZnO-GaN and conductivity of the GaN [86]. These results indicate the potential applications of the as-prepared metal oxide semiconductor based GaN in the sensing field [86]. Moreover, the study results showed that the FZnO-GaN designed sensor exhibited high response for 50 ppm C\(_2\)H\(_5\)OH gas at RT, with response-recovery time of 12 and 9 sec, respectively, which exceeded that of pure ZnO sensor [86]. Figure 37 shows the schematic illustration of electrodeposition of FZnO onto GaN and fabrication of FZnO/GaN gas sensors. Figure 38 shows the SEM images of FZnO/GaN gas sensors [86]. Figure 39 shows the XRD patterns of FZnO and FZnO-GaN. Figure 40 shows the response towards different concentrations of C\(_2\)H\(_5\)OH at 0, 33, 57 and 76% RH. Figure 41 shows the response curves of devices based on GaN, FZnO or FZnO-GaN. Figure 42 shows the schematic illustration of C\(_2\)H\(_5\)OH sensing mechanisms of FZnO-GaN.
The RT fast and reversible vertical-heterostructure diode gas sensor composed of reduced graphene oxide and AlGaN/GaN was investigated and reported by Bag et al. [88]. In that study, a vertical heterostructure diode (VHD) based on a van der Waals heterojunction between reduced graphene oxide (rGO) and AlGaN/GaN/sapphire was fabricated for use in the chemical sensing of toxic gases [88]. The study showed that the target gases interacted with the atomically thin reduced graphene oxide reduced graphene oxide layer, which served as a contact and sensing material; this interaction induced a change in the forward bias current of the vertical heterostructure diode through modulation of the effective Schottky barrier height (SBH) [88]. The study results showed that the vertical heterostructure diode gas sensor showed fast, repeatable, reproducible, recoverable, and stable RT operable gas-sensing performance for toxic gases, including nitrogen dioxide, sulfur dioxide, and ammonia [88]. Finally, the vertical heterostructure diode device has great promise as the fundamental structure of simple, low-power, low-noise, and RT operable chemical sensors. Figure 43 shows the schematic of rGO/AlGaN/GaN VHD gas sensor. Figure 44 shows the FE-SEM image showing post-reduction surface morphology of GO nanosheet directly coated on AlGaN surface. Figure 45 shows the repeatability of VHD gas sensor exposed to 150 ppb of (a) NO₂, (b) SO₂, and (c) NH₃ gases. Figure 46 shows the Variation of sensor current (Iₘ) values obtained at bias voltage.
The AlGaN/GaN-based pH sensors electrode free with and without a GaN capping layer was investigated and reported by Parish et al. [76,89]. In that study, the sensor exhibited a linear response towards pH variations when a GaN-capped heterostructure was used [89]. The study results showed that the difference in the response at low pH could be attributed to the difference in activity of surface donors (surface states) present for AlGaN/GaN heterostructures [89]. Moreover, the use of a GaN cap for electrochemical stabilization and degradation prevention at the surface means that the Coulombic interaction effects between the electrolyte and surface states are mitigated [89]. The study results showed that in the absence of a reference electrode, a linear response towards pH requires a GaN cap layer [89]. This behavior could be explained by the mitigation, when a GaN cap was used, of Coulombic interaction effects that occur between the electrolyte and surface states [89]. Figure 47 shows the schematic diagram for the (a) GaN/AlGaN/GaN device cross section and (b) device layout and measurement configuration for the (GaN)/AlGaN/GaN-based sensors. Figure 48 shows the normalized average drain-source voltage of AlGaN/GaN sensor.

The H₂ sensing properties of a novel metal-oxide-semiconductor (MOS) Pd/NiO/GaN-based MOS diode Schottky diode was investigated and reported by Liu et al. [90]. In that study, the MOS structure consists of GaN-based semiconductor system, a nickel oxide (NiO) layer, and palladium (Pd) catalytic materials [90]. In that study, the Pd/NiO/GaN-based diode showed several advantages in relation to H₂ sensing, including a simple structure, high sensing speed, wide flexibility for operation under both forward and reverse applied voltages, and a good sensing response [90]. The study results showed that the high sensing response was acquired in the same gas ambience under a reversed voltage of 2 V [90]. Finally, the Schottky diode sensor was a promising candidate for high-performance H₂ sensing applications [90]. Figure 49 shows the representative cross section diagram of the studied Pd/NiO/GaN MOS Schottky diode H₂ sensor. Figure 50 shows the I-V characteristics, under various concentrations of H₂ gas. Figure 51 shows the energy band diagrams of the GaN sensor. Figure 52 shows the forward sensing response of the GaN sensor. Figure 53 shows the transient responses of the GaN sensor.
The FET-like ammonia (NH₃) gas sensor based on a unique structure namely GaN honeycomb nanonetwork (GaN-HN) was investigated and reported by Shen et al. [91]. In that study, the utilizing of ohmic contact Ti/Al/Ti/Au multilayers as the source and the drain terminals and Pt nanonetwork layer as the gate terminal, the FET-like NH₃ gas sensors were fabricated by a two-mask photolithography process [91]. The study results showed that the fabricated NH₃ gas sensors had a high selectivity, fast response/recovery, and a wide detection range up to 5000 ppm [91]. The results also showed that the response and the recovery time for 5 ppm NH₃ gas were 23 sec and 101 sec at a moderate operating temperature of 120°C [91]. Figure 54 shows the SEM image of the GaN-HN sensor. Figure 55 shows the GaN-HN NH₃ gas sensor structure. Figure 56 shows the XRD pattern of the GaN-HN sensor gas. Figure 57 shows the I-V curve measured between the source and the drain without gate bias.
4. Conclusion

GaN offers some potential in providing nanostructured based gas sensors devices, and also encouraging progress has been made in the research phase. Despite this progress, there are still number of important issues that are in need of further investigation before this material can be transitioned to commercial use for the stated applications. The planar GaN based gas sensors have high restrictions to the detection of low gas concentrations. Moreover, GaN based sensors sensitivity, speed (response and recovery rates), selectivity, stability, reproducibility, durability, detection limit, and power consumption need more investigation and development. There is still much to be understood in terms of the mechanism of GaN based sensor devices specially for hydrogen gas sensors. Hence, the development of the high performance hydrogen gas sensors to continuously monitor the leakage of hydrogen and to accurately detect hydrogen concentration is an important and crucial issue in terms of environmental safety. Finally, although a number of GaN based sensors devices have been reported, there are some issues that need to be further investigation and study. These issues include the p-type doping, the lack of a credible p-type doping hampers widespread optical emitters in GaN.

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Figure 55. Structure of GaN-HN NH3 gas sensor [91]

Figure 56. XRD pattern of the GaN-HN sensor [91]

Figure 57. (a) I-V curve measured between the source and the drain without gate bias (b) In vs. Vg at various bias voltages Vg [91]
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