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RESEARCH ARTICLE

A STUDY OF THE CHARACTERISTICS AND SELECTION OF DOPED MATERIALS FOR NiO TO OPTIMIZE GAS SENSING

Monika Singh[1], Dr. Shriom Mishra[2], Dr. Shiksha Jain[2] and Mukul Saxena[3]

1. Student, Masters of Technology, Department of Electronics and Communications, IET, Ayodhya.
2. Assistant Professor, Department of Electronics and Communications, IET, Ayodhya.
3. Research Scholar, Department of Nanotechnology, Centre of Advanced Studies, Lucknow.

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Abstract

Gas sensing of hazardous has become a great challenge for several decades. Recently, technical and industrial advancements uninterruptedly produce the emission of hazardous and poisonous gases that are detrimental to human life; as a consequence gas detecting devices that are extremely sensitive and selective to such gases are in a high demand. Presently, gas sensors based on p-type NiO are attracting more attention, because of its outstanding repeatability, high specific surface areas, strong sensitivity, cheap cost and environmental friendly. Herein, we evaluated the various production techniques on p-type NiO nanostructures and their use as gas sensors. The basic gas sensing process linked to the p-type NiO is briefly described. The impacts of noble metals, transition metals, and transition metal dichalcogenide and phosphors materials on the NiO gas sensing performance are also examined in depth. With various level of doping, heterostructure NiO depicts improved sensing performance for gases like HCHO, NH_3, NO_2, C_2H_5OH and H_2. The arrangement of different semiconductor metal oxides to create heterostructures which further enhance the selectivity and sensitivity of the sensing parameters is also addressed. Heterostructure NiO has enhanced sensing capability for gases such as HCHO, NH_3, NO_2, C_2H_5OH, and H_2 with varying levels of doping. There are many literatures on heterostructures linked to NiO based sensor significantly in last decade. The current work will aid researchers in the selection of doped materials for NiO gas sensors in order to enhance sensitivity.

Introduction:-

Many of these gases can have both immediate and chronic health consequences [1, 2], thus rapid detection of flammable, poisonous, and exhaust gases is essential. In the automobile sector, manufacturing production, indoor air quality, and environmental monitoring, gas detectors have been widely used to monitor flammable, hazardous, and exhaust gases [3]. Because of the many uses that gas sensors provide, they are in high demand. They are dependable, low-cost, portable, and use little power. Because of their size-dependent characteristics, semiconductor metal oxides

Corresponding Author:-Monika Singh
Address: Student, Masters of Technology, Department of Electronics and Communications, IET, Ayodhya.

(SMO) are regarded to be promising among all available gas sensing materials. However, there are still important difficulties to be solved, such as high sensitivity, limited selectivity, stability, high operating temperature, and huge power consumption [4 - 6]. In practise, p-type SMOs have gotten very little attention for a long time. Because the p-type SMO is only beginning to be understood, additional research into the synthesis and/or design of highly sensitive and selective SMO-based gas sensors is needed [7, 8]. Because of its thermodynamic stability and distinctive optical, magnetic, and chemical characteristics, p-type nickel oxide (NiO) with a broad bandgap of 3.6 to 4.2 eV is the most remarkable material among the various SMOs [9 - 11]. By creating NiO nanostructures with a large surface area and gas diffusion, the gas sensing properties may be enhanced. As a result, one of the most important parameters to regulate during the creation of nanomaterials is morphological change [12-15]. Lu et al. [14] presented folding porous NiO nanosheets with excellent gas sensing behaviour, as an example. The gas sensing properties of NiO flake-flower structures produced using the sodium dodecyl sulfonate (SDS)-hydrothermal technique were investigated by Miao et al. [15]. The well-arranged flower-like NiO based gas sensor was extremely sensitive and selective towards ethanol vapour, according to these findings. Furthermore, previous studies [16] have shown that the water vapour in Ni doped SnO_2 based sensors interrelate with Ni related surface sites such as NiO clusters or Ni atoms contained within the SnO_2 surface lattice using the operando diffused-reflectance infrared Fourier transform infrared spectroscopy (DRIFT). They discovered that water vapour could not compete with CO for pre-adsorbed oxygen ions, and therefore its interfering effects on CO sensing were much reduced. Pascariu et al. [17] investigated the electrical properties of NiO–SnO_2 nanofibers under humidity impact and discovered that they may be utilised as active nanostructures for humidity sensors.

This review considers the effects of doping, heterostructures on NiO gas sensing. Furthermore, a review of papers based on NiO sensors since many years reveals that interest in heterostructures, as opposed to undoped or doped NiO, and the use of a hydrothermal synthesis technique and so on, has been steadily rising on the issue.

Gas Sensing Mechanism of NiO

To detect the composition and concentration of gas, gas sensors use chemical and physical processes to transform gas into electrical signal output. Gas sensors are commonly employed in the detection of flammables, explosives, poisonous and dangerous gases, and environmental management [18]. The majority of gas sensors in recent years have been surface-controlled resistance sensors, in which the sensitive materials of semiconductor resistance gas sensors are mostly concentrated in metal oxide semiconductors [19]. Because of a huge number of free electrons in the conduction band and oxygen vacancies on the metal semiconductors' surfaces. The material surface of metal semiconductors has strong adsorption properties and high reactivity, and is altered by the action of surface gas due to a large number of free electrons in the conduction band and oxygen vacancies on the surface. As a result, electrical characteristics may be used to make measurements [20]. Metal oxide materials offer excellent physical and chemical characteristics, are inexpensive to create, and are easy to prepare.

SMO's gas sensing characteristics are based on a change in charge carrier concentration caused by an interaction between the target gas and the surface of SMO. Furthermore, the oxidation-reduction interactions of the chemisorbed oxygen with the detected gases on the surface regulate the gas sensing properties of SMO. SMO charge carrier concentration in ambient air is a major determinant of the gas reaction [21, 22]. A SMO is dropped over two or more electrodes (platinum (Pt) electrodes) in chemoresistive-type sensors to assess the variation in the behaviour of the SMO's electrical resistance in the presence of the target [23, 24]. When a p-type NiO with holes as the majority carrier is exposed to clean air (21% oxygen), electrons are removed from the NiO and attracted to the oxygen species, which is chemisorbed on the sensing material's surface. More holes are created, resulting in an increase in electrical conductivity and the formation of the depletion layer. With increased electron flow, the potential barrier height at the grain boundary is reduced, resulting in a high sensor current flow (low sensor resistance) in a reasonably clean air environment [25, 26]. The accompanying diagram depicts the relevant interaction on the SMO surface and with the adsorbed oxygen species.

$$O_{2(gas)} + e^- \rightarrow O^-_{2(adsorbed)} \quad (\text{Top} < 100\ ^0\text{C})$$

$$O_{2(gas)} + 2e^- \rightarrow 2O^-_{(adsorbed)} \quad (100\ ^0\text{C} < \text{Top} < 300\ ^0\text{C})$$

$$O^-_{2(adsorbed)} + e^- \rightarrow O^-_{2(adsorbed)} \quad (\text{Top} > 300\ ^0\text{C})$$

In general, the adsorbed oxygen is strongly influenced by the operating temperature (Top): O_2 nature less than 100ºC, O- between 100 and 300 ºC, and O_2- greater than 300ºC [26, 27]. When CO, H_2S, ethanol, or NH_3 are introduced to a p-type NiO SMO, the molecules are adsorbed on the surface and they give electrons to the MOX by interacting with the chemisorbed oxygen ions. Electrical conductivity diminishes when the number of holes decreases and the depletion layer thickens (high electrical resistance). This extension of the depletion layer causes an increase in the potential barrier height at the border location. The analyte gas interacts with the chemisorbed oxygen ions on the surface and removes electrons from the metal oxide in the case of oxidising gases such as CO_2, O_2, and NO_2. Electrical conductivity increases as the number of holes increases and the depletion layer thins (low electrical resistance).

Table-1: A literature survey on NiO/doped Nio gas sensing for various gases

Material	Gas Analyst	Conc. ppm	Operating Temperature	Response	Ref.
NiO nanosheets	Ethanol	50	250	65	28
NiO	acetone	100	260	13.51	9
NiO flake-flower	Ethanol	400	300	32	29
NiO nanoflower	Ethanol	200	300	40	30
NiO	Benzaldehyde	100	300	250	31
NiO-SnO2 nanoflower	Ethanol	20	320	94.8	32
NiO-RuO_2	Ethanol	1000	350	29.1	33
NiO-SnO_2	Formaldehyde	100	200	27.6	34
NiO:Ce Nanoparticles	NO_2	40	150	29	35
NiO thin Films	H_2	3000	175	65	36
NiO thin films	NO_2	20	150	2.6	37
NiO	H_2S	100	150	9.0	38
Zn-doped NiO	CO	200/400	300	-	39
Al-doped NiO	Ethanol	100	200	12	40
In-doped NiO	Methanol	200	300	10.9	41
Sn-doped NiO	Xylene	100	225	20.2	42
Nio activated coal	CO	100	100	125	43
NiO-graphene	H_2	2000	350	68	44
Cr-doped NiO	Xylene	50	325	88	45
Fe-Doped NiO	Ethanol	100	280	12	46
Ce-Doped NiO	Trimethylamine	10	160	12.8	47
Pt-doped NiO	NO_2	40	150	29	48
Au@NiO	NH_3	1000	300	1278	49
W-NiO	Ethanol	100	200	2.54	50
Pd-NiO	O-xylene	15	RT	0.19	51
Sn-doped NiO	Xylene	1	300	65.4	52
Zn-doped NiO	Formaldehyde	1.4	200	136	53
Sn-doped NiO	Ethanol	100	340	15.6	54

Ethanol (C_2H_5OH) sensing using NiO

This paper describes a simple and flexible method for producing macroporous p-type metal oxide thin films. Colloidal templating and RF-sputtering, followed by heat treatment, were used to create two-dimensional arrays of p-type NiO films with a hollow hemisphere shape. The NiO hemisphere's diameter and shell thickness were 800nm and 20nm, respectively. Close-packed arrays of hollow NiO hemispheres were discovered to have p-type gas sensing characteristics against (CO, H_2, C_3H_8, CH_4, NO_2, and C_2H_5OH), with considerably improved responses to C2H5OH (Rgas/Rair = 5.0 at 200 ppm). [53]

A hydrothermal reaction of $NiCl_2$ with NaC_2O_4 and H_2O in the presence of ethylene glycol (EG) and subsequent annealing at 400 C in air were used to create NiO crystallites-based nanowires with various aspect ratios. The hydrothermal reaction temperature and duration were adjusted to control the aspect ratios of NiC_2O_4•$2H_2O$ precursor nanowires in the range of 11–1050. The gas-sensing capability of as-prepared NiO nanowires with various aspect ratios was tested in the presence of toluene, ethanol, acetone, triethylamine, and methanol. It was discovered that increasing the aspect ratios of NiO nanowires enhanced gas-sensing capability. [54]

Based on an efficient interaction of Kirkendall effect and volume change post phase transformation, a new method was used to manufacture porous NiO nanotubes with controlled internal voids. Nickel nanowires were chemically transformed into Ni_3S_2/Ni core shell structures for this purpose, followed by a controlled oxidation, which resulted in a 1D porous structure with voids due to the accompanying volume change (Ni f NiO conversion). The pattern formed, with interpenetrating gaps and surface porosity, resulted in a large specific surface area of 161.6 **m2 3 g** 1. The gas sensing characteristic of such a double-walled structure was discovered to change with the concentric vacuum between the core and the shell. Measurements of gas sensing in a hollow porous core shell The high sensitivity of NiO nanotubes to ethanol was due to effective adsorption of target molecules in the inner voids and their fast diffusion and transport across the porous structures. [55]

Nickel oxides (NiO) nanowires were produced using the nanocasting method using ordered mesoporous silica SBA-15 as hard templates, and then mesoporous NiO nanowires (NiO MNWs) were separated from dispersed NiO nanowires (NiO DNWs) by centrifugation. To analyse the phase structure and microstructure, XRD, TEM, nitrogen adsorption/desorption isotherm, and UV–vis spectrum were employed. Both samples were found in bundles with varied grain sizes, and NiO MNWs with bigger grain sizes had a greater percentage of mesopores. For the higher mesoporous-structure, NiO MNWs had a larger specific surface area (92.61 m^2/g) and bandgap (3.31 eV) than NiO DNWs. As a result, the NiO MNWs-based sensor demonstrated high sensitivity and rapid response-recovery to ethanol at 340^0C. The gas-sensing capabilities of NiO MNWs were superior than those of NiO DNWs, which can be attributed to their larger surface area and wider bandgap. [56]

Hydrogen (H_2) Sensing using NiO

The characteristics of hydrogen sensing in nanocrystalline NiO thin films are studied. NiO thin films were made using a sol–gel technique, with specific attention paid to changing the porosity of coated films through a multi-step coating and annealing procedure. The experimental results showed that multi-step annealed NiO thin films had greater porosity than films made using a standard sol–gel method. The grain size of NiO films grew as their thicknesses increased, but the sheet resistance of the film dropped. For two stacked samples, the greatest gas reaction was found at 175^0C. NiO films formed by multi-step annealing demonstrated a greater sensitivity to hydrogen than NiO formed through a conventional sol–gel method. The H_2 gas reaction was reduced as the thickness and porosity of NiO sheets were increased. A repeated annealing procedure yielded a high response value of 68 percent for 3000 ppm of H_2 at 175^0C for an optimised sample. The influence of humidity on the sensor's gas detecting capability was investigated, and the devices were tested for multiple cycles to determine the sensors' repeatability. The cross sensitivity studies revealed that the sensor may be utilised to detect hydrogen in a reducing gas combination. [57]

An intriguing nickel oxide (NiO) thin film-based hydrogen sensor device is researched and shown, which was created using a low-powered (50 W) radio-frequency (RF) sputtering technique. The investigated device exhibits improved performance, including a very high hydrogen sensing response ratio (416 (DR/R)), an extremely low detecting limit (50 ppm H_2/air), a fast sensing response speed (7 s), a lower operating temperature (&350^0C), and a broad sensing range of hydrogen concentration ($50e^{10,000}$ ppm H_2/air). Furthermore, the gadget has the advantages of low cost, ease of manufacturing, and chemical stability. [58]

A binary, nanostructured carbon-nanotube (CNT) sheet covered with nickel oxide (NiO) was created to be used as a hydrogen (H_2) sensor. Thermal annealing was used to increase the sensor's sensing capabilities at room temperature. To explore the influence of the sensing material's surface area, NiO particles of various sizes were electrodeposited onto CNT sheets, which is a straightforward technique for binary composites. After thermal annealing, we discovered a considerably greater sensitivity at ambient temperature. Furthermore, the size of the NiO particles has a considerable impact on the sensor's sensitivity. [59]

The development of low-cost, high-performance hydrogen gas sensors is gaining popularity due to its advantages in detecting hydrogen leaks early. The in-situ synthesis and decorating of Pd nanocrystals (NCs) on the surface of mesoporous NiO nanosheets for efficient hydrogen gas sensor application is described here. The utilisation of a large specific surface area of mesoporous NiO nanosheets and the catalytic activity of Pd NCs are crucial aspects in improving hydrogen gas-sensing capabilities by improving the contact between the hydrogen molecule and the sensing surface. The mesoporous NiO nanosheets were created using a surfactant-free hydrothermal technique followed by thermal oxidation, whereas the Pd NCs were decorated using in-situ palladium complex reduction. Several sophisticated methods were used to examine the crystal structure and growth process of the materials. The gas-sensing experiments indicated that the Pd-NiO nanosheets-based sensor detected hydrogen at low concentrations efficiently, with rapid response, high sensitivity, and stability. [60]

Methanol (HCHO) Sensing using NiO

The sensing mechanism of p-type semiconducting NiO thin films exposed to formaldehyde is discussed in this study. The effect of sensing layer thickness and annealing treatment on sample structural, optical, and electrical characteristics is investigated. Temperature-stimulated conductance measurements are used to assess the height of the potential barrier. The potential barrier height is proportional to the amount of oxygen ionosorption on the semiconductor surface. In addition, Fourier transform-IR research was performed to establish the chemical processes that regulate the gas detection process and the temperature range in which they occur. As a consequence of the research, it is feasible to describe how sample thickness and annealing treatment impact the sensing mechanism. [61]

Nickel oxide (NiO) thin films were evaluated against low quantities of formaldehyde in this study (HCHO). RF reactive magnetron sputtering in an argon/oxygen mixed environment was used to produce NiO thin films on alumina substrates. On the reverse side, a Pt heating resistor was placed for precise temperature control. In order to stabilise the microstructure of the samples, they were annealed in synthetic air for 4 hours at 700ºC. To investigate the effect of this parameter on both the microstructure and sensor response, two different thicknesses (150 and 300 nm) were deposited. For 150 and 300 nm-thick samples, the optimum working temperatures were determined to be 340 and 300 $_o$C, respectively. For a set of HCHO values ranging from 5 to 20 ppm, lower thickness samples had a better sensitivity. Furthermore, the reproducibility of the tests for the most sensitive samples was evaluated. [62]

A simple and reliable method for mass producing hollow NiO microspheres built from nanosheet-stacked nanoparticles is devised. A hydrothermal process without surfactants or chemical additives was used to create the $Ni(HCO_3)_2$ precursor with a hollow spherical shape. The gas bubble formed by the reaction might serve as a template for the production of $Ni(HCO_3)_2$ hollow microspheres. Upon calcination, they are transformed into hierarchical NiO hollow microspheres built from nanoparticles (with a diameter of y25 nm), which are further

assembled by stacking ultrathin nanosheets. The sensing capabilities of hierarchical NiO hollow microspheres were investigated. They have a high sensitivity, quick response and recovery durations, and excellent n-butanol response and recovery properties. When compared to NiO nanoparticles of comparable size (y20–35 nm), the nanoparticle formed NiO hollow microspheres had improved gas sensing capabilities. The efficient integration of several nanostructures in a single micro unit would give a unique approach to designing new materials for nanodevices. [63]

At ambient temperature, single-crystalline b-$Ni(OH)_2$ ultrathin nanosheets were created by a simple electrochemical reaction of Ni electrodes with a mixed solution of NaCl, NaOH, and NH_4Cl. The typical thickness of b-$Ni(OH)_2$ nanosheets is 1–15 nm, which is easily adjustable by varying the quantity of NaCl. The mechanism for the production of nanosheets is believed to be the selective adsorption of NH_3 molecules on the (001) crystal face of b-$Ni(OH)_2$, which inhibits growth in the [001] direction. Thermal breakdown of b-$Ni(OH)_2$ nanosheets in air at 400 µC for 2 hours resulted in porous NiO ultrathin nanosheets. The gas detecting characteristics of NiO ultrathin nanosheets were studied, and the sensors demonstrated excellent sensitivity, low detection limit, and wide dynamic range for formaldehyde detection. [64]

Ammonia (NH_3) Sensing using NiO

The study and demonstration of an intriguing ammonia gas sensor based on a p-type NiO thin film produced by a radio frequency sputtering method. When compared to conventional n-type metal-oxide sensors, the studied device exhibits comparable and good sensing performance, including a high sensing response ratio of 289 percent, a shorter response time of 31 s, and a shorter recovery time of 78 s under an introduced 1000 ppm NH3/air gas at 250 and 350 °C, respectively. Furthermore, at 250 °C, the investigated sensor device has a lower detection limit (5 ppm NH_3/air). [65]

Metal–oxide heterostructures are critical materials for the development of different harmful gas/chemical detection sensor systems. However, important sensor characteristics like as sensitivity, selectivity, stability, responsiveness, and recovery periods must to be improved for actual technological applications. Because of their surface chemistry, low-dimensional materials have demonstrated enormous promise to tackle the majority of essential challenges. The role of a nanostructured n-ZnO/p-NiO heterostructure as a room temperature (RT) ammonia sensor is explored in this study. The electrospinning method was used in this study to create heterostructure metal–oxides mixed with polyvinyl alcohol (n-ZnO/p-NiO) nanofibers. [66]

Semiconductor NiO two-dimensional grainy films on glass substrates are demonstrated to be ammonia-sensing devices with great overall performance, including strong stability, fast reaction time, remarkable recovery performance, sensitivity, and selectivity. The morphology and structural study of gas sensing materials revealed that the as-fabricated NiO films had a homogeneous and highly ordered porous structure on substrates, consisting of tiny particles with sizes ranging from 8 to 30 nm. These particles' shells were ultrathin amorphous NiO plates, while the cores were face-centered cubic single crystal structures. We discovered that the excellent electron transport and interconnection properties of sensing films improved the stability and recovery performance of sensors, and the porous surface structure increased the specific surface area of sensing films, resulting in fast response and excellent sensitivity for sensors in gas sensing performance tests. Meanwhile, this sensor showed a high selectivity for ammonia, which may be attributed to NiO-sensing films greater binding affinity for electron-donating ammonia. [67]

Chemical reduction with magnetic fields and subsequent heat treatment technique were used to create NiO p-type semiconducting nanowires with aspect ratios up to 2000. NiO nanowires have a diameter of around 150 nm and a length of up to 300 mm. At atmospheric pressure, Ni nanowires were created from a framework of Ni nanospheres. By experiencing an amorphous oxidation process, Ni nanowires were transformed into NiO semiconducting nanowires by an in situ chemical oxidation process in open air. The grain size in the NiO nanowire structure is significantly influenced by heat treatment. NiO nanowires with crystalline grain sizes of around 12 nm have a band

gap energy of about 4.20 eV, which is higher than the band gap energy of bulk NiO. (3.65 eV). Meanwhile, we discover that the optical band gap energy steadily increases as the crystalline grain size decreases. [68]

An electrolytic method coupled with subsequent high temperature oxidation was used to effectively manufacture nanoscale Zn-doped NiO dendritic crystals with a Christmas-tree-like shape. The trunks are 6–10 mm long with sizes ranging from 190 nm to 200 nm, while the branches are 1–3 mm long with diameters ranging from 150 nm to 180 nm. The sensor with doped NiO dendritic crystals responded 5–8 times quicker and recovered 30–50 times faster than the sensor with pure NiO dendritic crystals, which is essential for the practical use of this NiO sensor. [69]

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Nitrogen Dioxide (NO_2) Sensing using NiO

For the first time, nickel oxide (NiO) nanoflowers were successfully produced using a solution plasma method from a combination of $Ni(NH_3)_6^{2+}$ and triethanolamine. X-ray powder diffraction, scanning electron microscopy, nitrogen adsorption–desorption isotherms, and transmission electron microscopy were used to analyse the as-prepared samples. A potential formation is based on the experimental results. Furthermore, the gas reactions of NiO nanoflowers to 100 ppm of a range of gases, including H_2, NO_2, CO, toluene, NH_3, and H_2S, were studied at 150 °C. NiO nanoflowers were discovered to be potential NO_2 sensing materials due to their high responsiveness and selectivity. [71]

Using lotus pollens as bio-templates, chemicalbath deposition was used to create hierarchically porous NiO microspheres with interconnecting nano-pores. The resulting NiO microspheres have a specific surface area of 95.58 m^2/g and an average pore size of 20.98 nm, making them excellent for gas sensing. To improve performance, the NiO microspheres were further decorated with Pd/PdO, and the sensor based on the Pd-decorated NiO microspheres exhibited high sensitivity (S = 203), quick response/recovery (73 s/169 s), and good selectivity to 1.8 ppm NO_2gas at 250 ^oC. [72]

A simple hydrothermal method was used to create hierarchical -Fe_2O_3/NiO composites with a hollow nanostructure. By growing -Fe_2O_3 nanorods on the surfaces of porous NiO nanosheets with a thickness of 12 nm, hierarchical -Fe_2O_3/NiO composites were created. A static system was used to study the gas sensing characteristics of hierarchical -Fe_2O_3/NiO composites toward toluene. At 300 °C, the response of -Fe_2O_3/NiO composites to 100 ppm toluene was 18.68, which was 13.18 times greater than pure NiO. [73]

There has been a surge of interest in the synthesis of reduced graphene oxide (rGO)–metal oxide semiconductor (MOS) nanocomposites for room temperature gas sensing applications in recent years. In general, the incorporation of rGO can obviously improve the sensitivity of a MOS. However, a lack of understanding about how rGO can improve the gas-sensing performances of MOSs limits its sensing applications. An rGO–NiO nanocomposite was synthesised in order to gain insight into the sensing mechanism of rGO–MOS nanocomposites and to improve the sensing performances of NiO-based sensors at room temperature. [74]

Conclusion and Remarks

The production of p-type NiO-based gas sensors using different techniques, including hydrothermal/solvothermal, sol-gel, chemical/co-precipitation, and microemulsion, was discussed. It was also discovered that, among the different synthesis techniques, a significant amount of work on NiO-based sensors has been done using the hydrothermal approach. Various morphologies with relatively large surface areas due to doping provided sufficient adsorption sites for all involved molecules in a small space, which improved sensing in most cases. The formation of a p-n heterojunction at the interface between p-type NiO and n-type MOX had a high energy, and therefore may serve as an active site for catalyzing the breakdown of analyte gas molecules. Heterostructure NiO has enhanced sensing capability for gases such as HCHO, NH_3, NO_2, C_2H_5OH, and H_2 at different levels of doping. The synergistic impact of NiO and other MOX was also one of the elements that contributed to the improved sensing mechanism. This review study showed that there has been little work done, particularly in the area of doped materials for NiO sensors and their reaction to different gases.

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