Chapter

Metal Oxide Gas Sensors by Nanostructures

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Abstract

Recently, metal oxide gas sensors by nanostructures have stirred interest and have found their way in many applications due to their high sensitivity, material design compliance and high safety properties. Gas performance tests of n-type ZnO, Al-doped ZnO and ZnO/MWCNT structures toward different type gases from our previous studies have been reported. It is indicated that nanoparticle formations on the film surfaces, grain sizes, gas types and operating temperatures have a severe effect on the chemisorption/physisorption process. Low concentration detection, determination of grain size limit values and reducing operating temperature to room temperature are already obstacles on long-life sensitivity and long-term stability characters. Doping is an effective way to increase gas sensitivity with atomic surface arrangement and active gas adsorption sites, which are generated by doping atoms. However, C-based material/MO nanostructures are preferred than doped MO films with their working even at room temperature. Up to now, a lot of methods to improve the gas sensitivity has been proposed. With the help of the development of surface modification methods such as different types of doping and MO-C composite, sensitivity, which is the most important parameter of sensor performance, can also be stable as well as increasing later on.

Keywords: metal oxide, gas sensor, toxic gas, doping, multiwalled carbon nanotube

1. Introduction

Increased environmental pollution, numerous motor vehicles, factory wastes and urbanization factors have been the source of high increases in the release of toxic, explosive and flammable gases in the environment of developed countries. High rate of gas emissions has both a negative impact on human/animal health and it can also have bad consequences on the environment and natural resources from day by day.

With the start of the Industrial Revolution, the acceleration of coal and mine quarries caused a significant increase in deaths due to toxic gas. First, canaries were used in gas detectors in mines. The cost and difficulty of using different methods for determination of toxic gases have revealed the gas sensors. In 1815, British scientist H. Davy developed a gas meter called 'Davy's lamp' against methane gas [1]. In 1926, Johnson produced the first commercial catalytic, combustion gas sensor, and in 1929, the company they founded with Williams became the first company in Silicon Valley in electronics [2].

Gas sensors are used to detect combustible, explosive and toxic gases, when the measured gas concentration exceeds the threshold value they can give an alarm (sound, signal, etc.) that can be used as portable or fixed devices. The most important part of this device production is the sensor which determines 4S parameters (sensitivity, selectivity, stability, speed). Apart from them, recovery time, response time and power consumption are also other parameters. The sensor part records changes in the physical conditions or chemical components as signals (permeability, resistance, temperature, acoustic wave, capacitance, etc.) as a result of interaction between target gas and surface atoms (O^-, O^{2-}, H^+ and OH^-) by absorption/desorption of gas on the material surface at a specific operating temperature. Signal can correlate concentration of target gas [3].

The recent change in the OSHA Time Weighted Average (TWA) Permissible Exposure Limit (PEL) is 25, 35 and 1 ppm for NH_3, CO and NO_2 gases, respectively [4].

CO is a toxic colorless gas, environmental pollutant and kills by causing hypoxia with damaged hemoglobin cells in the blood. In general, the measurement of CO gas is realized by detection of percentage of carboxyhemoglobin in the blood. Another important issue is creation of residential and automotive environment so it is so necessary fast and sensitive detection. Difficulty in detecting very low levels and continuous CO formation in the air poses problems [5].

Odorless and toxic ammonia (NH_3) combustion, which is used in a large area as a fertilizer, refrigerant material and household cleaning product, is a major hazard. Using or producing ammonia besides any uncontrolled leaks by the infrastructures or its explosion causes health hazards. In addition, it is a chemical pollutant in the production of silicon type devices in clean room [6].

Nitrogen dioxide (NO_2) is a volatile and toxic gas. It has hazardous effects in environment as a secondary pollutant and its detection is so important. NO_2 gas generates fuel burning at high temperature and in nitrogen cycle, including acid rains. Under even very low concentrations (<10 ppm) it causes serious damages for human health such as throat discomfort, transient coughs, eye irritation, fatigue and nausea [7].

With nano-sized designed gas sensors, surface to volume ratio is increased for absorbed target gas as well as higher efficiency is obtained than traditional bulk-scale designed devices, because different atomic coordination and translational symmetry at the surface ensure electrical properties changing in semiconductors [8]. In particular, a dramatic increase using the nano-sized designed gas sensors have been observed in industrial areas such as pharmaceuticals, medical, automotive, building automation, space tools, wearable devices. The first study of the semiconductor material group was given by Brattain and Bardeen on germanium (Ge) in 1953 [9]. In the next study, in 1954, Heiland had a research report on the gas sensitivities of metal oxides, and also in 1962 Seiyama showed that ZnO structures were sensitive to reactive gases in the air [10]. In 1968, Taguchi-type sensors were introduced to market and metal oxide (SnO_2) gas sensors were moved to industrial level [11].

Nano-scale designed gas sensors are usually classified depending on measurement data as follows; (i) chemiresistors, (ii) thermal conductivity gas sensors, (iii) acoustic wave gas sensors, (iv) calorimetric gas sensors, (v) optical gas sensors (vi) electrochemical gas sensors and (vii) infrared absorption gas sensors [13, 14].

Chemiresistive gas sensor working principle can be explained simply as adsorption of electron with target gas on the surface can cause charge transfer (a change in charge carrier concentration) between target gas/material surface region (receptor function) so electrical properties can be (resistance or conductivity) increase or decrease. Easy measurement with two electrodes is a factor in their preference and supplying safety.

Today, using chemiresistive metal oxide (MO) semiconductors, real-time gas sensor has gained great importance both in the science/industrial world due to their high sensitivity to chemical environments, low price, simple implantation, safety and durable to high temperature/high pressure, indicating that compelling conditions. Companies such as FIS, Mics, UST, CityTech, Appliedensors and Newcosmos produce millions of MO gas sensor per year, especially the Figaro company which produces Taguchi type sensors [15].

Gas selectivity is a critical problem for metal oxide gas sensors. To increase the selectivity of metal oxide sensors, it is proposed to use a heating mode of a gas-sensing floor with rapid temperature modulation in the last studies.

Metal oxide semiconductor gas sensors are focused on different and new materials at room temperature with the increasing need for faster, more precise and easy gas sensing, as showed in **Figure 1**. Thus, the most important parameter mechanism is gas sensitivity, which still does not reveal the exact reasons (strongly related to surface reactions), can be detailed. Production techniques (spray pyrolysis, pulsed laser deposition, magnetron sputtering, spin coating, and chemical bath deposition) are undeniable facts because structure parameters, grain boundaries, point defects, surface morphology, porosity, etc. must be affected. Additionally, reducing (H_2, H_2S, etc.)/oxidizing (NH_3, NO_2, etc.) gas types and p- or n-type is also effective on the chemiresistive MO performance, as showed in **Figure 2**. Oxidizing or reducing gas is associated with electron affinity, which is compared to the work function of most metal oxide so in the case of oxidizing gas, the adsorbed gas molecules on the surface of the MO are anions.

The change in electrical resistance of semiconductors can be explained as follows; formation of the space-charge depletion zone on the surface and around the particle and the energy band bending. Surface energy barriers with variable heights and widths depend on the relationship between charging the surface states of the adsorbed species for conduction electrons. In gas sensors using n-type semiconductor oxide, it has been observed that the resistance of the oxide increases with the interaction of gases such as O_3 or NO_2, while the resistance decrease of the oxide occurs with interaction of gases such as CH_4 and CO, as showed in **Figure 2**.

It is discussed that resistive-type metal oxide semiconductors produced by nanostructures (especially thin films) in detail toward NH_3, NO_2 and CO gases. Additionally, effect of doping and nanocomposite forming with C-based material (especially carbon nanotubes) were studied.

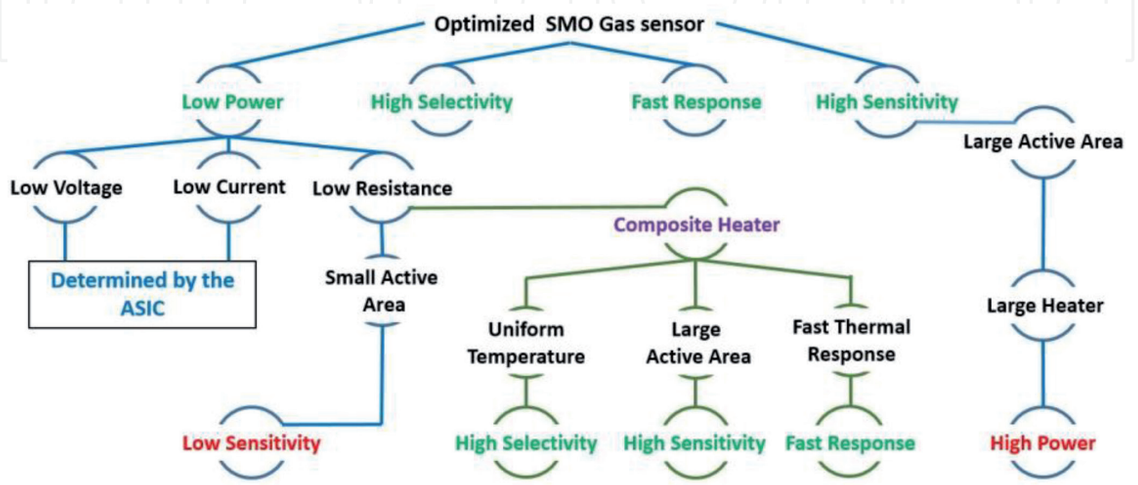

Figure 1.
Advantages and disadvantages of semiconductor metal oxides (reprinted from study of [12] with their permission).

Type of Sensitive Material	Type of Aimed Gas	Response(S)
n-type	oxidizing	R_g / R_a
	reducing	R_a / R_g
p-type	oxidizing	R_a / R_g
	reducing	R_g / R_a

Figure 2.
Sensitivity measurement of material type and target gas type (reprinted from study of [16] et al. with their permission).

2. Metal oxide (MO) gas sensors

Since 1962, the addition of the oxygen contained in the metal oxides to the reaction so increase of reactions and their stable chemical transduction properties which can reversibly convert chemical reactions on a surface make the metal oxides attractive for detect various harmful, toxic, and explosive gases. Development of gas sensors, which are almost 21% of the metal oxides used in the field, is rapidly increasing [17]. Because they have unique properties such as low cost, long lifetime, fast response time and relatively high sensitivity. However, some restrictions are detected in these structures such as background gas effect, poor selectivity and power consumption in high temperature conditions which could not be proper for especially wireless applications.

Basically, the main challenge is they operate only at elevated temperatures and consume more power with high operating temperatures. Physisorption and chemisorption are surface adsorption forms of oxygen. Physisorption to chemisorption needs activation energy with realized by increasing operating temperature. In addition, forming of oxygen species depends on the operating temperature substantially. Sun et al. reported that molecular species are more than atomic species below 150°C, this cause a decrease in gas sensitivity [18].

Another goal of gas sensitivity works is to ensure that electrical change in the gas environment occurs not only at grain boundaries but on the entire material surface. Since grain boundaries are smaller than MO particles, surface chemistry is more effective and the effect of grain boundaries on electrical change is not considered.

To achieve high performance from MO gas sensors, detailed knowledge of the gas sensing mechanism is essential. In general, it can be explained as follows; oxygen adsorption on the surface of sensing material, adsorbed oxygen species (extrinsic surface acceptor states) molecular (O_2^-) or atomic (O^-, O^{2-}), captured from the interior of the sensing material, resulting in a depletion layer on the surface due to oxygen species. Eventually observing a decrease in the conductivity/resistance [19]. In other words, oxygen ions on the surface of metal oxides are highly active interactions with the target gas molecule. When O_2 molecules adsorb from the surface of the MO, they break off electrons from the conductivity band (E_i) and trap electrons form on the surface, which come across in ion form. This causes band bending and electron depletion layer (space charge layer) formation. When the electron concentration in the conductivity band decreases, the conductivity decreases as well. At the same time, negatively charged traps in these different types of adsorbed oxygen cause downward bending of the band curve, which, compared to the flat state of the band, decreases conductivity. The thickness of the electron depletion layer is the width of the band bending region. The displacement of adsorbed oxygen with other molecules and the reaction of different oxygen ions with reduced gas changes conductivity.

Among metal oxide gas sensors single (ZnO, NiO, TiO_2, SnO_2, WO_3, etc.), binary and ternary samples have unique properties such as chemical stability, relatively low harmful for environment, abundant in nature and low cost. Wang et al. showed that metal oxides selected for real gas sensors can be separated according to their electronic structure [20];

a. d^0 transition metal oxides: In this group (WO_3, V_2O_5, TiO_2 and etc.), d^0 electronic configurations are preferred with their wide band gap energy and surface forms so it can measure easily.

b. pre-transition metal oxides: In this group (Al_2O_3, MgO and etc) are not preferred due to neither electrons nor holes forming so occurs very band gap energy, structural instability and difficulty of measure electrical conductivity.

c. post-transition metal oxides: They have d^{10} electronic configuration. ZnO, SnO_2 Ga_2O_3 and In_2O_3 are preferred in MO gas sensor applications. Because they are so proper for electron accumulation and chemisorption of donor-like species occurrence.

3. Thin film metal oxide gas sensors

In semiconductor gas sensor applications, advantages of thin film using are low resource waste, high surface/volume ratio, low power consumption, easy compliance with integrated circuits and easy alteration of electrical properties with changing film production parameters. Thin film technology allows the film properties to be changed by keeping the thickness parameter under considerable control. In this way, thin films are easily integrated into the device during the material production process. They can also be used as electronic circuit elements by acting as new materials when they are produced in multilayer.

Thin film metal oxides are used by the detection a lot of gas types such as Carbon-based (CO, CO_2, CH_4, C_2H_5OH, C_3H_8), nitrogen-based (NH_3, NO, NO_2), H_2, H_2S, ethanol, acetone, LPG and moisture.

The large number of grain boundaries in thin film polycrystalline MO's limits mobility, thus reducing carrier concentration and decreasing gas sensitivity. The presence of depletion layers in these grain boundaries is the most important factor that reduces mobility. Grain boundaries affect mobility due to their positioning to potential barriers with high intensity defect levels.

There have been a lot of ZnO thin film study to detect NO_2 gas sensing that have been reported with different morphologies nanowires, nanorods [21], nanoprisms [22] and nanospheres [23] in order to enhance surface area. In 2019, Duoc et al. synthesized ZnO nanowires and nanorods with using on-chip grown via hydrothermal method at room temperature NO_2 gas sensing [24]. The diameter of these structures severely affected gas sensing, indicating nanowires were more sensitive than nanorods. ZnO nanobarded fibers were synthesized by electrospinning and chemical bath deposition. These structures showed improved NO_2 detection performance for gas concentrations up to 30 ppb [25].

In our previous study, nanoflower shaped n-type ZnO films synthesized by chemical bath deposition and their 0.5 ppm NO_2 gas sensing was detected, showing in **Figures 3** and **4** [26]. Operating temperature was chosen at 200°C due to statical recovery kinetics were worse under this temperature. Oxygen vacancies (oxygen-deficient ZnO) acted as adsorption sites, electron donor sites and nucleation centers for small metal clusters. Reaction on the ZnO film surface was given by two

equations between exposing oxidizing type NO_2 molecules and oxygen species in the ZnO grain boundaries;

$$O_{2(ads.)} + 2e^- \leftrightarrow 2O^-_{(ads.)} \quad (1)$$

$$NO_2 + O^- \rightarrow NO_3 + e^- \quad (2)$$

With increasing annealing temperature and thereby decreased grain sizes caused an increase surface/volume ratio and NO_2 gas sensing, as expected for n-type ZnO. It was interesting that very high annealing temperature (>500°C) could lead to deterioration on the substrate/deposited layer interface, as showed in **Figure 3d**.

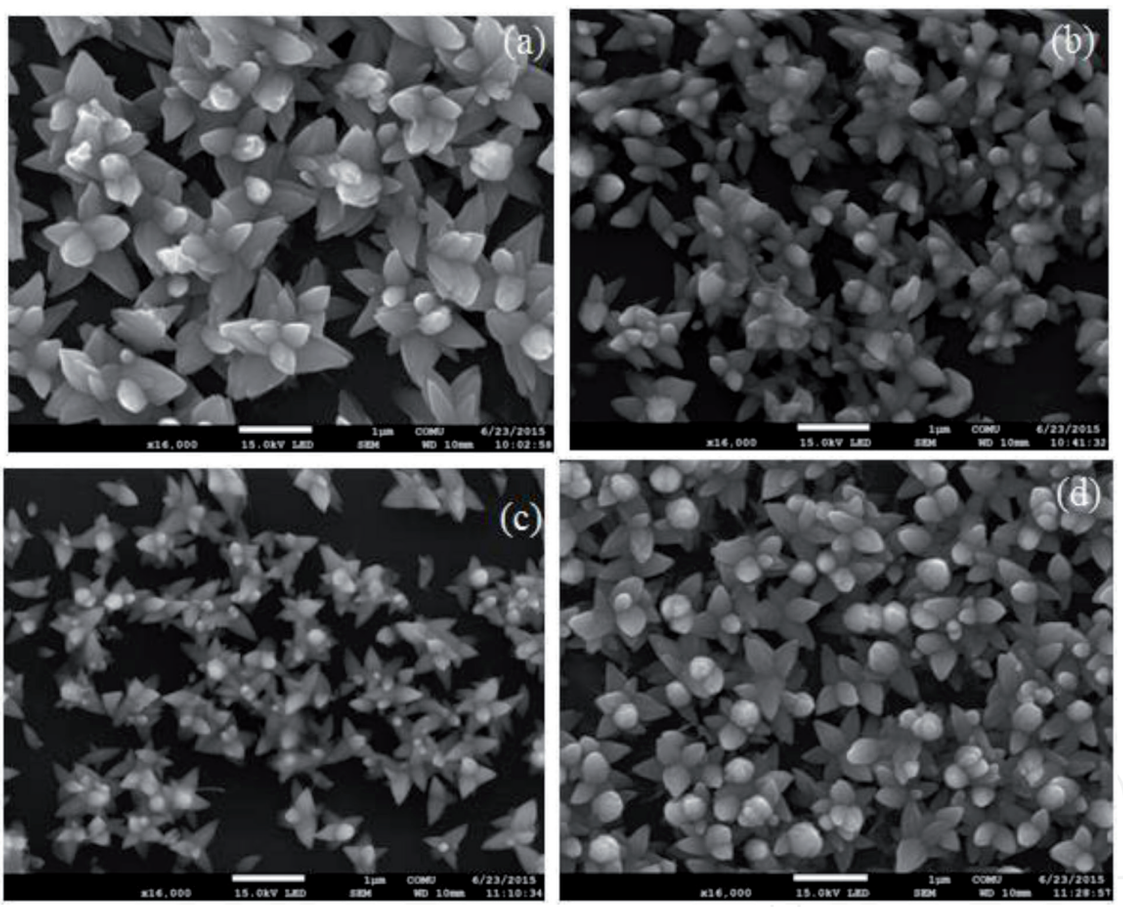

Figure 3.
SEM images of (a) ZnO and annealed ZnO films at (b) 450°C, (c) 500°C and (d) 550°C (reprinted from [26]).

4. Doping

To arrangement structural, morphological and gas sensing properties of MO nanomaterials, doping is an effective method with metallic ions (Al, Fe, Co, Cu, Ag and etc.). Defect sites and location of a host or doping ions determines grain size and electronic band of nanomaterials thereby sensing layer resistance. The substituted atoms can act as reactive sites for gas adsorption [27]. On the other word, surface impurities and defects with generating doping ions and thereby adsorption sites can cause extrinsic electronic states [28]. The reduction of the grain size to nanometers or to a scale comparable to the thickness of the charge depletion layer

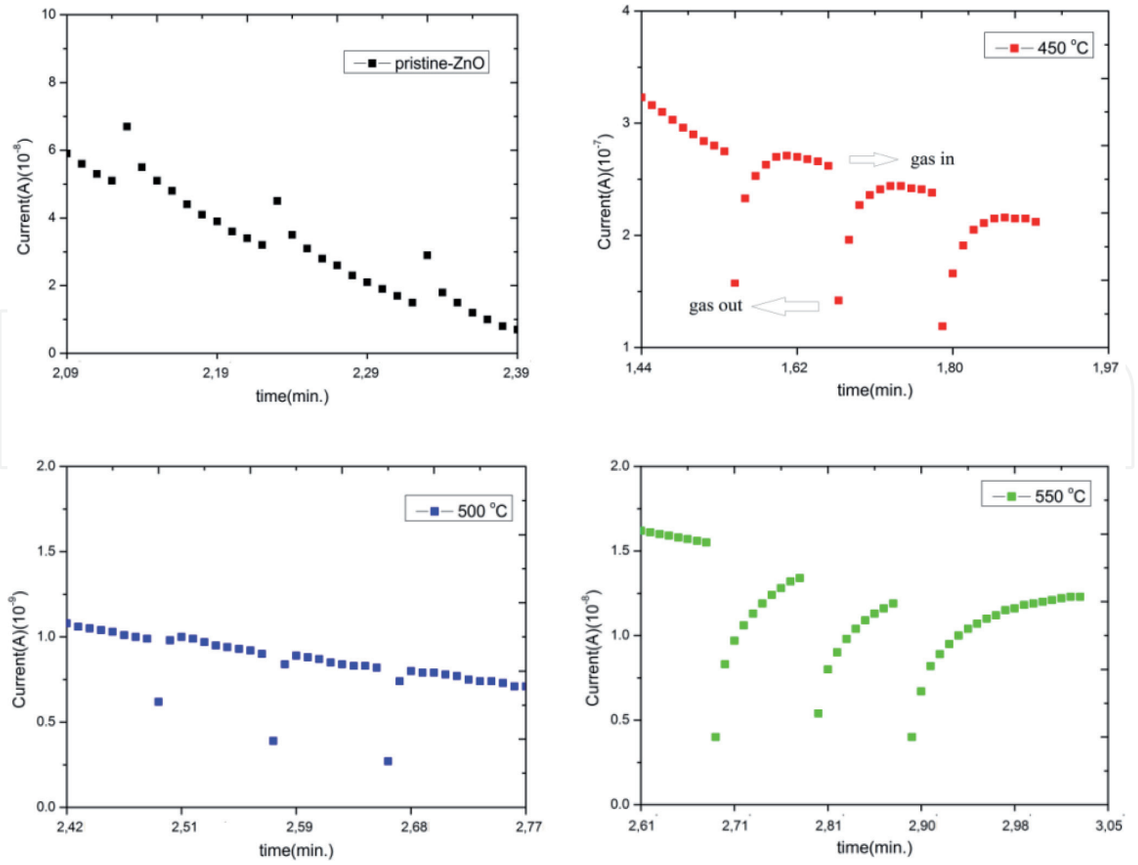

Figure 4.
0.5 ppm NO_2 gas sensitivity of ZnO thin films at 200°C (reprinted from [26]).

leads to a dramatic improvement in the gas sensitivity. It has been also found that the crystal structure of the grains affects the absorption of gases. Metal atom doping can also increase gas selectivity as reported by Govardhan and Grace [29].

Ionic radius difference plays a very important role between metal dopant and host metal (Zn, Sn, Fe, etc.) in gas sensing. Interstitial sites and oxygen vacancies are so critical in physisorption and chemisorption processes. To determine electronic traps in the doped structure deep level transient spectroscopy is an effective method.

However, heavily doped metal oxides (>10%) showed poor gas performance with high concentration defect regions, which is attributed to limitation on the Fermi level shift during interaction with the target gas [30].

The highest surface roughness values are 5% Al doping, and samples with this dopant have the highest NH_3 response times, explained by Aydın et al. [31]. Other Al:ZnO film studies were received by Dimitrov et al. [32] and Patil and Sondkar [33] toward CO gas.

In our previous study, Al-source effect was investigated on the NH_3 gas sensing and response time parameters as showed in **Figures 5–7** [34]. Alteration of surface particle type and dissolve depending on Al-source were caused by gas sensing parameters severely due to changing the energy-band gap structure, surface effective/contact area and NH_3 gas adsorption rate. Oxygen molecules that are adsorbed convert into oxygen species depending on temperature by capturing free electrons from the oxide. Then, depletion layers form in surface areas, leading to an increase in oxide resistance. According to Eq. (3), the electrons were released back to the conduction band, finally resulting in the decrease of the resistance.

$$2NH_3 + 3O^- \rightleftarrows N_2 + 3H_2O + 3e^- \quad (3)$$

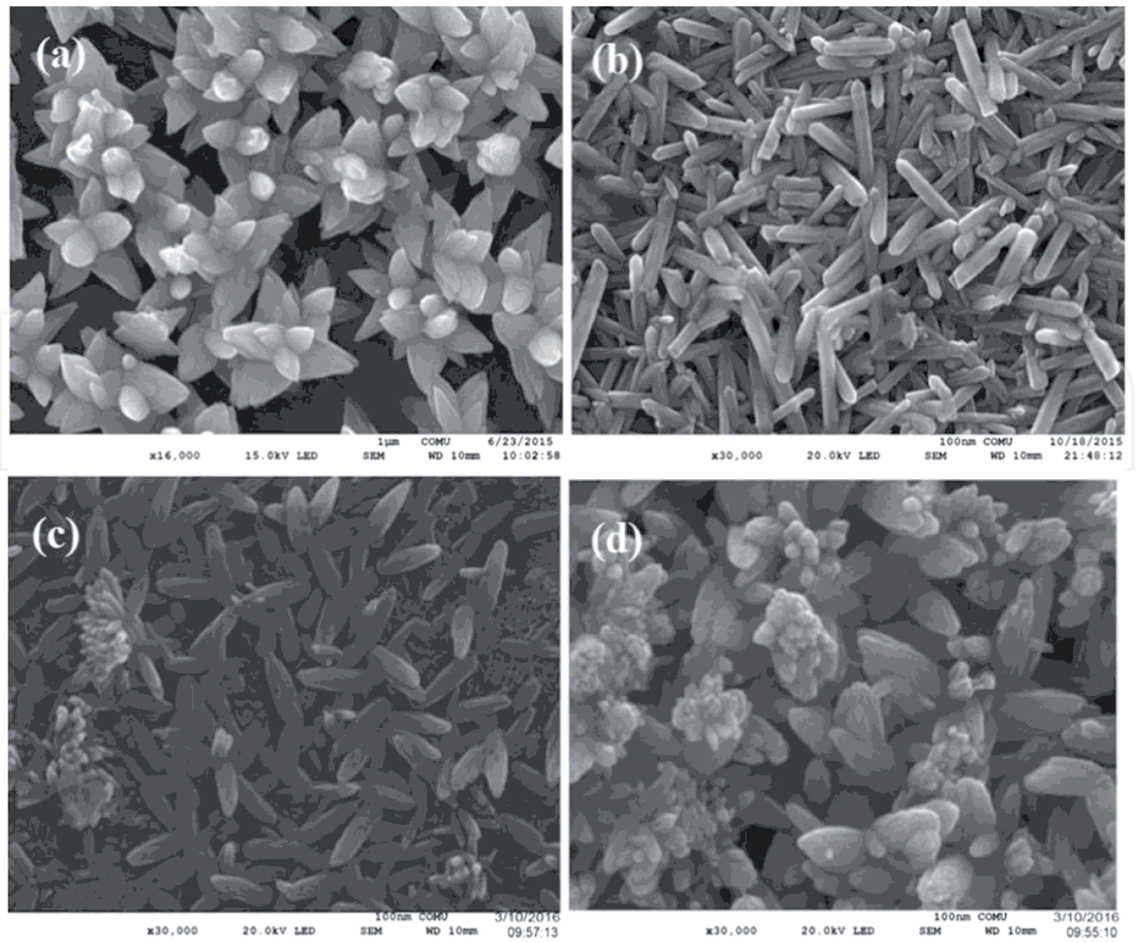

Figure 5.
SEM images of (a) pure ZnO and (b, c, and d) different Al:ZnO films depending on Al-source reprinted from [35].

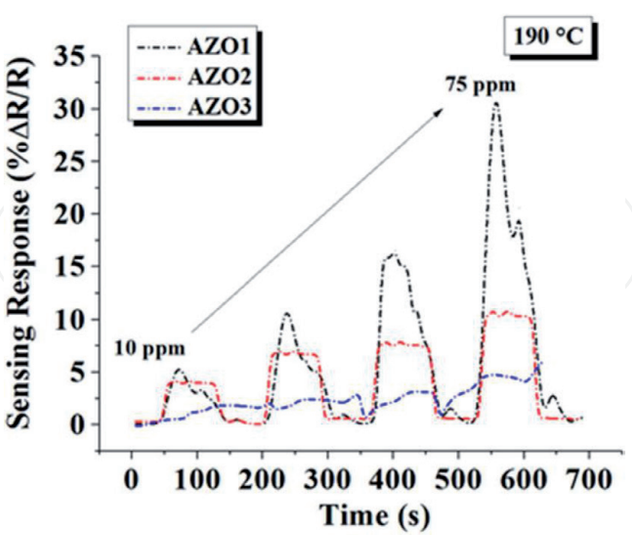

Figure 6.
NH_3 sensing response of Al:ZnO films as a function of time (reprinted from [34]).

As showed in **Figures 5** and **6**, nanorod formations (**Figure 5b**) had highest response times and gas sensing at low temperatures in powder Al-source used samples. Al-sources have high impact on gas sensing character due to changing film growth process and surface morphologies.

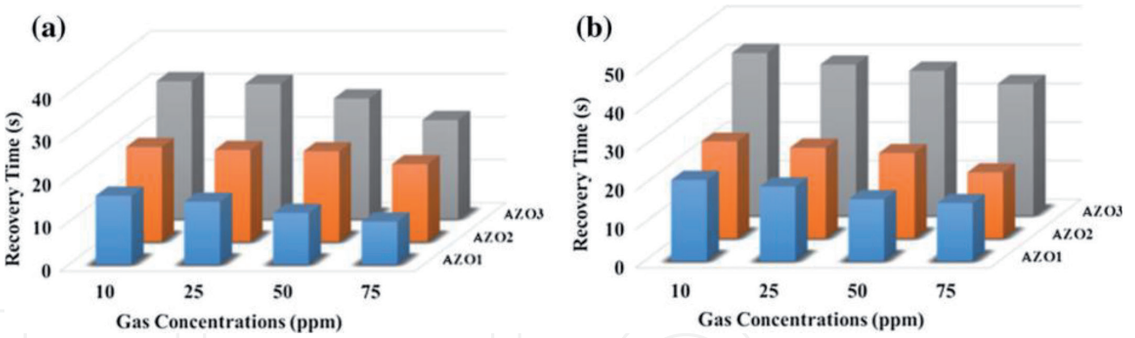

Figure 7.
(a) NH_3 gas response and (b) NH_3 gas recovery times of Al:ZnO films (reprinted from [34]).

5. MO/CNT nanocomposites

The exceptional and unique properties of carbon-based materials (carbon nanotubes, graphene, graphite, and plumbane) offer a great advantage for the production of improved composites, while their applications as a matrix element depends primarily on the relationship between the matrix and the other material. Gas sensor sensitivity of some MO-C-based nanostructures (MO: ZnO, SnO_2, TiO_2) is showed in **Table 1** and SWCNT-MO structure studies are so rare until now, interestingly. Because SWCNTs are much more expensive than MWCNTs and titanium oxide film production is usually expensive by physical methods. Defects forms such as atom vacancies, functional groups and stone wall defects on nanotubes can enhance the sensitivity toward different gases with metal oxide compositions. Additionally, as a matrix material supplies high quality of crystal lattice leading to a quite low electronic noise and they act as the Schottky barrier. These defect sites lower the activation energy barrier thus enabling chemisorptions of analytes on the surface of CNTs and make room temperature measurements possible [35].

In general, incorporation of C-based material into MO structure, n-type to p-type convert or p-n junction are observed so active sites available for gas adsorption and formation desired depletion layer [36].

Another improvement mechanism approach at room temperature proposed by Tai et al., indicating that supporting role of MO nanoparticles layer (first

	NO_2 gas sensing	NH_3 gas sensing	CO gas sensing	References
Graphene-ZnO	17.4 (100 ppm)	1.25 (10 ppm)	23.5 (1 ppm)	[36–38]
Graphene-SnO_2	2.45 (20 ppm)	1.9 (500 ppm)	9 (400 ppm)	[39–41]
Graphene-TiO_2	—	1.7 (10 ppm)	6.5 (100 ppm)	[42, 43]
MWCNT-ZnO	1.025 (10 ppm)	41 (10 ppm)	—	[44, 45]
MWCNT-SnO_2	2 (10 ppm)	1.06 (60 ppm)	0 (100 ppm)	[39, 46, 47]
MWCNT-TiO_2	—	2 (100 ppm)	7 (50 ppm)	[48, 49]
SWCNT-ZnO	6 (250 ppm)	—	0 (50 ppm)	[50, 51]
SWCNT-SnO_2	11.1 (10 ppm)	50 (100 ppm)	1.29 (50 ppm)	[52–54]
SWCNT-TiO_2	—	—	—	—

Table 1.
Comparison of some MO/C-based nanostructure gas sensors sensitivity (S%) toward NO_2, NH_3, and CO gases.

depletion layer from adsorption of ionized oxygen) as well as formed accumulation heterojunction at interface between MO and C-based material (second depletion layer) [37].

In a recent study, Lee et al. explained that improvement mechanism that was attributed the removal of oxygen-containing functional groups, the supply of electrons from the oxygen vacancies of ZnO material, and the formation of C-O-Zn bonds in ZnO-rGO membrane and operation under 100 ppm NO_2 at room temperature [55].

Among C-based materials, two types of carbon nanotubes (CNTs) (both single-walled [SWCNT] and multi-walled [MWCNT] carbon nanotubes) are so attractive in gas sensor support material studies due to their room temperature gas sensing, fast response and good reversibility properties. Hollow cores and inner/outside walls of CNTs supply large gas adsorption regions so they allow donating/withdrawing charge carrier mobilization [56]. Therefore, it causes a change in charge carrier concentration.

Multi-walled carbon nanotubes (MWCNTs) are nanoscale materials that comprise of several concentric single walled carbon nanotubes (SWCNTs) and exhibit diameters in the range of 5 and 30 nm [57]. Purification of MWCNTs (acid treatment, oxidation by heating, filtration, centrifugation, size-exclusive chromatography, etc.) is a preferred method to observation of no signal between target gas/CNT surface [58].

Sputter of nanoclusters of proper type atoms on surface provides catalysis process, enhancing gas sensing with functionalization of CNTs [59].

As reported to our previous study, MWCNT coating and MWCNT etching with HCl acid treatment effect was investigated on nanoflower ZnO seed layer against CO gas, showed in **Figures 8** and **9** [60]. The gas-sensing results had been shown that the response had been dramatically enhanced with the decoration of MWCNTs and rMWCNTs/ZnO sensor had exhibited the highest response to CO gas at 70°C. Consequently, it had been determined that gas sensing performance of the MWCNTs-decorated ZnO sensors had improved surface reactions with ZnO lattice. This may be attributed to the diffusion of the target gas through MWCNTs nanochannels.

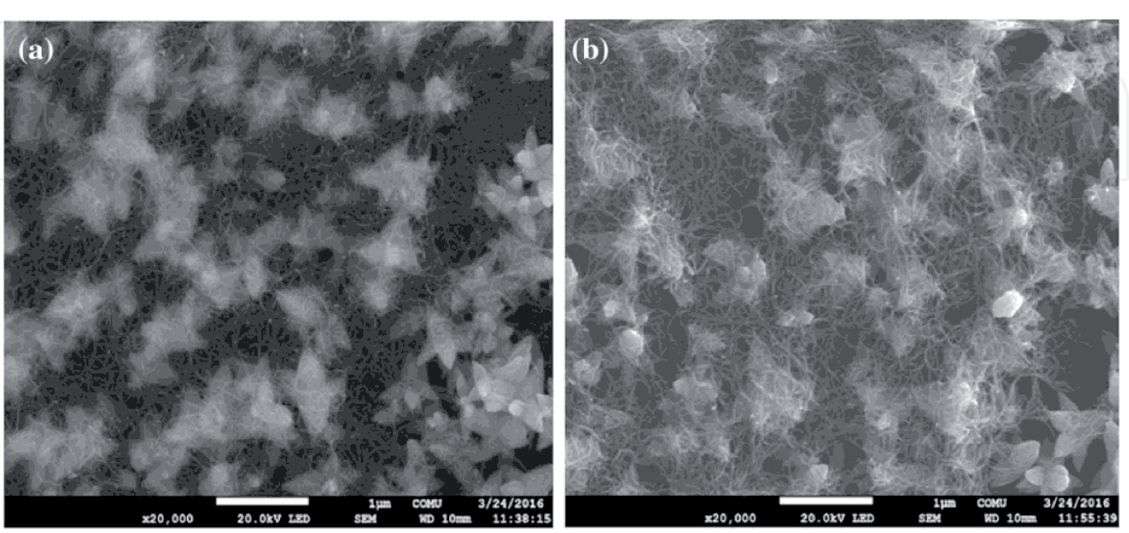

Figure 8.
SEM images of (a) ZnO/MWCNT and (b) ZnO/etched MWCNT films (reprinted from [60]).

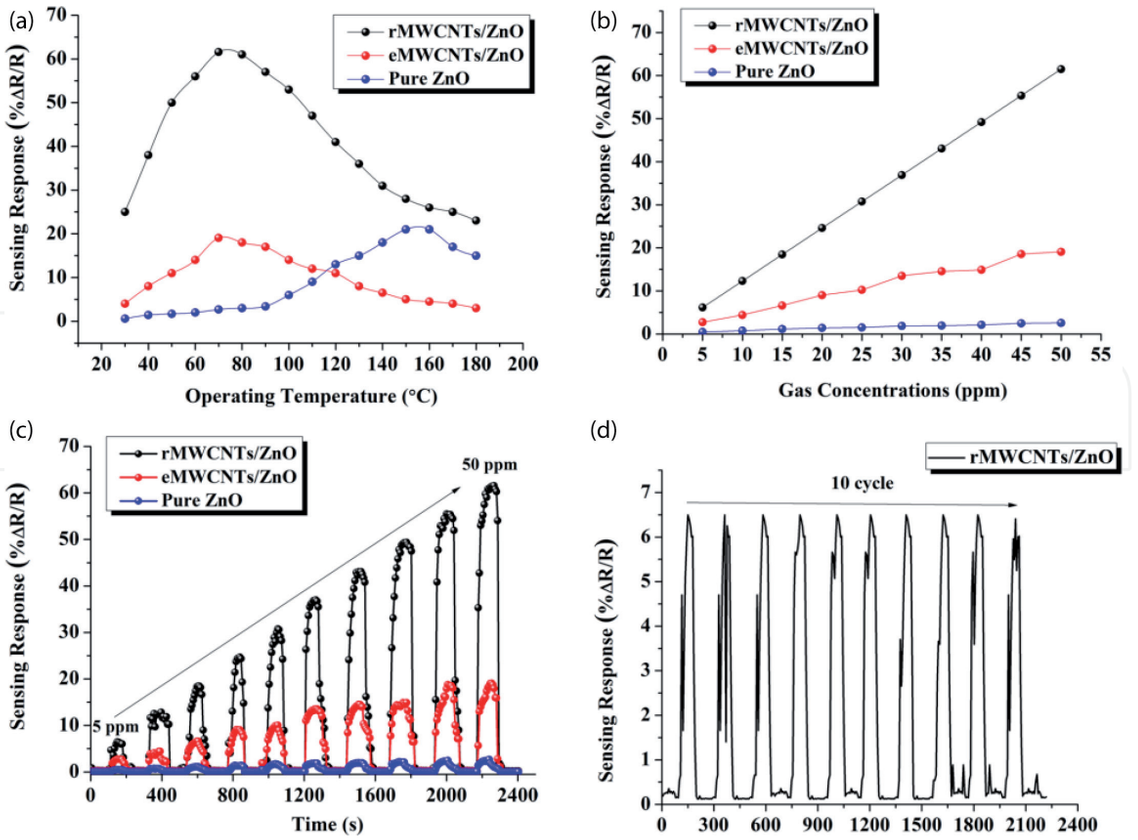

Figure 9.
Gas sensing parameters of ZnO/MWCNT film (reprinted from [60]).

6. Conclusion

In global, gas sensor market demands high performance on all 4S parameters (most common from ppb to ppm), miniaturization of weight, compatibility with other device components/wireless, flexibility for especially wearable devices and fabrication cost. It is expected to reach nearly 3 billion dollars in 2027. Recently, chemiresistive metal oxide semiconductor gas sensors are so interesting due to low cost, relatively high sensitivity and easy integration with CMOS compatible devices. The fact that the metal oxide gas sensor studies are very wide and there are quite a lot of publications in the literature about this topic. Hence some limitations are obligatory in this chapter.

Unlike other gas sensors in chemiresistive gas sensors, target gas concentration variation can be done in a quantitative way by direct measurement of electrical resistance. A change in the barrier height occurs between the particles due to the reducing or oxidizing of target gas. This detection largely depends on the grain size, depletion layer width and conduction characteristics of the nanostructures. Debye length must be compatible to the depletion layer.

Long-life sensitivity is still a key challenge. Today, the first and most common approach can be given as rapid decrease of material dimension (3D to 1D) and thus it has rapid expansion on the sensitive region but other factors (background gas, grain boundaries, granular forms, humidity and etc.) can be disregarded. Additionally, minimum particle size and enhanced/tunable surface reactivity at room temperature are main goals in a lot of studies. However, particle stability thereby gas sensing performance is not stable especially with particle size changing.

Gas transfer via micro-, meso-, and nano-porous sensing films with their assembled hierarchical, hollow, and yolk-shell forms has an enormous effect on interaction of target gas-oxygen species-nanoparticles.

In this study, metal oxide gas sensors by nanostructures were investigated comprehensively. ZnO nanoflower, Al:ZnO depending on Al-solution type and ZnO/MWCNT films were investigated toward different gases from our previous studies. Gas sensitivity was preferred main gas sensor parameter.

The results show that there is an interaction between the gas molecules and the sample surface based on the exchange of charges. While there is no gas in the environment, O_2 molecules adsorbed on the sample surface form an electron depletion zone. When the sample interacts with gas molecules, O_2 molecules also interact with the gas, and O_2 molecules begin to be dislocated from the surface. By separating O_2 molecules from the surface, electrons are released according to the property of the gas (reducing or oxidizing), or an electron is ionized from the sample. Thus, the change in electrical conductivity is observed. The detection rates and return mechanisms of the samples have also been fairly quick. Return times indicate that the main mechanism between the gases and the sample surface is physical adsorption. In physical adsorption, gas molecules are held in structurally formed cavities on the surfaces of the container in which they are located, interacting with the surface atoms Van der Waals. This phenomenon is reversible.

In MO and metal doping MO studies, film growth process must be under control to avoid agglomerative formations and un-expected ion positions in crystal structure, this causes gas adsorption process decreasing. Similar effect also occurs in C-based material/MO nanocomposites however having bonds of C-based materials and p- to n-type conversion/p-n junction have improvement effect on the gas sensitivity with expanded depletion region, indicating room temperature sensing.

On the other hand, in improvement studies of gas sensors, metal oxide gas sensors based on micro-hotplates fabricated with micro-electro-mechanical system (MEMS) technology that needs to be developed due to being restrictions on material and design. Uniform mesoporous structures are also desirable because they allow more sensing regions for gas diffusion. Additionally, metal organic frameworks (MOFs) with ultrahigh porosity have been also so attractive especially last years.

Considering the circumstances mentioned above, engineering control over the metal oxide structure and sensor design is so critical in order to obtain high stability as well as high gas sensitivity. Development of new metal oxide material compositions and their high stability/crystallinity will bring high performance gas sensors. New nanofabrication techniques and surface improved studies have contributed to development metal oxide gas sensors.

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