Impact of Doping on Gas Sensing Properties of Metal Oxide Semiconductor: A Review

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Abstract: The impact of doping on the gas sensing properties of Metal Oxide Semiconductors (MOSs) is studied in this review work. It gives a detailed comparison of several characteristics (sensor response, sensitivity, selectivity, response time, and recovery time) that influence the performance of MOS-based gas sensors. The changes in MOS materials used for gas sensing induced by dopants or impurities are discussed in this paper. Dopants change the microstructure and morphology, electrical characteristics, electronic structure, crystalline lattice, crystallite size, surface area, and band gap of metal oxide semiconductors, hence improving their properties for gas sensing applications. Dopants can cause MOS flaws by producing oxygen vacancies or creating solid solutions in some conditions. These flaws improve the gas sensing properties, which have been briefly discussed. Finally, the current review paper explains the gas sensing mechanism of pure and doped MOSs for oxidising and reducing gases.

Keywords: Doping, Metal Oxide Semiconductors, Crystallite size, Surface area, Sensors.

1. Introduction:
The development of efficient gas sensors for the detection of harmful gases is essential because of the rising concentrations of hazardous gases in the environment through industrial, inorganic farming, automobiles, etc. A gas sensor is a device that gives information about the chemical composition of its surrounding atmosphere. The physicochemical features of the metal oxide sensitive layer (such as mass, temperature, and electric conductivity) change reversibly when it interacts with chemical species (adsorption, chemical reaction, and electron transport). These changes are converted into an electrical signal, such as frequency, current, voltage, or impedance/conductance, which is then read and subjected to additional data compression and processing. Different materials, such as metal oxides, carbon nanotubes, organic compounds, and ceramic compounds, can be used to develop gas sensors [1, 2].

1.1 Overview of Metal Oxide Semiconductors:
Brattain and Bardeen demonstrated in 1953, over 68 years ago, that gas absorption on the surface of a semiconductor can induce a change in the material's resistance, Seiyama et al 1962 and Taguchi 1970 have made a consistent and effective effort to employ this change for gas detection [2, 3]. Metal oxides are one of them, and because of their great stability, sensitivity, and ability to detect a wide variety of target gases, they are regarded as viable materials for gas sensor applications. Metal oxide gas sensors have some disadvantages, such as slow response, low conductivity, required high operating temperature, and sluggish recovery speed. Gas sensors based on Metal Oxide Semiconductors have been used in the household and industrial settings to monitor flammable and dangerous gases. Gas sensors are in high demand because of their wide range of applications and their low cost, reliability, small size, and low power consumption [3, 4]. Metal Oxide Semiconductors (MOS) are divided into two types: n-type and p-type. The bulk of charge carriers in n-type MOS are electrons, whereas charge carriers in p-type MOS are holes. When exposed to the target gases or humidity, MOS-based sensors work on the concept of resistance changes. Oxidizing gases cause an increase in n-type semiconductor resistance and a decrease in p-type semiconductor resistance, while reducing gases do the opposite. When p-type films are exposed to oxidising gases, resistance reduces, while resistance increases when exposed to reducing gases. When exposed to oxidising gases, the resistance of n-type films rises, while resistance reduces when exposed to reducing gases. Free electrons are created when the target gases react with oxygen species [4-6]. N-type MOS has better sensitivity to target gases than p-type MOS, although p-type MOS has its own benefits such as good catalytic characteristics and lower humidity and working temperature dependence [7, 8]. Traditional fabrication technologies have improved, allowing low-cost sensors with good response and reliability to be produced. The goal of researchers has been to develop a highly sensitive gas sensor with a quick response and recovery time. Operating temperature, specific surface area, crystalline size, crystalline structure, and resistivity qualities all have an impact on the sensing performance of MOS gas sensors. To enhance these properties of MOS, much research has used doping processes during the last few decades. Over the decades,
doping and imperfections have played a significant role in optimizing material structural, electrical, optical, and mechanical characteristics. We are mechanical properties by manipulating the fundamental structure at the nano-scale, due to the implementation of sophisticated production and characterization technologies. To tackle technological, economic, and environmental concerns, such research and inventions are essential [9, 10].

1.2 Classifications of Metal Oxide Semiconductors:
MOSs are often categorized based on their bandgap energy and electronic structure, which makes them ideal for gas detection as shown in figure 1.

![Fig. 1: Classification of metal oxide semiconductors](image)

According to the response of the targeted gas, metal oxide semiconductors are also divided into two major categories. The first is an n-type MOS, and the second is a p-type MOS. The bulk of electrons and a smaller number of holes make up an n-type semiconductor. Metal oxide semiconductors of the n-type include ZnO, MgO, In$_2$O$_3$, Al$_2$O$_3$, and CO$_3$O$_4$. Similar to n-type semiconductors, p-type semiconductors have a majority of holes and a few of electrons. CuO, TeO$_2$, Y$_2$O$_3$, La$_2$O$_3$, NiO, CeO$_2$, Mn$_3$O$_7$; these are only some few p-type metal oxide semiconductor examples. Figure 2 depicts the classifications of MOS gas sensors based on variations in resistivity [3].

![Fig. 2: n-type and p-type metal oxide semiconductors](image)

1.3 Nanomaterials of Metal Oxide Semiconductors:
Due to their size dependent features of MOSs with sizes ranging from 1 nm to 100 nm are rapidly being employed for gas sensing. For MOSs gas sensors, humidity is a critical factor. The sensitivity of metal oxide sensors is reduced when humidity increases. High selectivity is one of the issues faced by semiconductor metal oxide gas sensors. Improving the selectivity of an MOS gas sensor can be done in two ways. The first is to develop a material that is selective for a single component and has very low or no cross-sensitivity to other compounds present in the working environment. The second method is to discriminate between many analytes in a mixture, i.e. doping. The selectivity of
gas sensors is also improved by adding dopants or impurities to metal oxides. The performance and efficiency of sensors are improved by dopants/impurities [6, 11, 12].

1.4 Role of Doping in Metal Oxide Semiconductors:
Doping can be defined as the addition of impurities to a pure material. Metal, metal oxide or other impurities can be found as dopant. Dopants are frequently used to change the grain boundary energy. It’s possible that the dopant is only partially soluble in the primary component. In-situ and ex-situ doping techniques are used to accomplish the doping procedure. In situ usually refers to ‘in the reaction mixture’. In situ processing is a method of doing many procedures on a wafer without exposing it to air in between. In order to reduce the number of particles, the approach also seeks to minimize wafer handling. The fabrication of elevated source/drain junctions for deep submicron MOS transistors is one of the most promising in situ processing applications. In the In-situ technique, doping is carried out during synthesis of nanoparticles, and in the Ex-situ technique, doping is carried out after synthesis of nanoparticles, i.e., addition of dopant in the function material by weight method [13- 15]. It is well known that doping rare-earth metal oxides into nanocrystalline titanium dioxide films enhances photovoltaic and photocatalytic efficiency. Doped films have been found to be 40–50 times better conductive than undoped films, with linear current–voltage characteristics and lower light sensitivity than undoped films. Due to a decreased charge trapping rate in the deep trap regime, cyclic voltammograms of doped materials exhibit elevated scan rate dependence [16]. Guo, Qingchuan, et al. prepared polymer composite by using in situ and ex situ methods of for a particular application. Author reported prepared nanocomposites refractive index can be tuned by increasing the TiO$_2$ concentration using both in situ and ex situ methods [13]. The addition of dopants or impurities to metal oxides, or the synthesis of mixed metal oxides, improves the selectivity of gas sensors because each material is selective to particular gas species. Dopants and impurities increase sensor reliability and productivity [16]. There are several methods for optimizing gas sensor parameters. The sensor’s sensitivity can be considerably increased by modifying the parameters such as morphology, grain size. Because the Schottky barrier at grain borders limits conductivity, sensitivity is decreased for larger grains with D >2L. Conductance is confined by grain necks when D=2L, and it is impacted by each grain when D=2L. There are three main mechanisms for grain size first is D >> 2L denoted grain boundary control, second is D = 2L denoted neck control and third is D< 2L indicating grain control as shown in figure 3 [5, 18].

![Fig. 3: Mechanisms of grain size](image)

Different nanocomposites/nanostructured can be compared in terms of their electrical properties, structural qualities such as grain size and particle size, gas sensitivity, selectivity, reaction time, and recovery time. Metal oxide gas sensors’ sensitivity will be improved by adding dopants at specific quantities. The activity of additives, such as dopants in metal oxide materials, is essentially attributable to two mechanisms that may be responsible for increased gas sensing. The first one is a chemical method, which is typically employed in spillover operations, and the second is an electronic method [18, 19].

1.5 Nanocomposites of Metal Oxide Semiconductors:
Metal oxide composites, also known as nanocomposites, are formed by mixing two or more metal oxides to improve performance over single metal oxides. The response of some sensors made composed of two metal oxides is better than that of individual materials. The reversible interface of the gas with the material surface has been demonstrated by various researchers to be a feature of conductometric semiconducting metal oxide gas sensors. Many variables, both internal and external, can impact this response, such as natural qualities of base materials, surface areas and microstructure of sensing layers, surface additives, temperature and humidity, and so on. In recent years, numerous publications on metal oxide gas sensors were published. Sensitivity, as one of the most essential properties of gas
sensors, has gotten a lot of attention recently, and there has been a lot of effort put into improving gas sensor sensitivity [19-21].

2. **Gas sensing mechanism of metal oxide semiconductors**

Metal oxide semiconductors (MOSs) are widely used in gas sensors due to their sensitivity and selectivity towards various gases. The gas sensing mechanism of MOSs is primarily based on changes in the electrical conductivity of the material when it comes into contact with specific gases [23, 24]. MOS gas sensors operate by exploiting the changes in electrical conductivity that occur when specific gas molecules adsorb onto the surface of the metal oxide semiconductor. This change in conductivity is used to detect and measure the concentration of gases, making MOS sensors valuable for various applications such as environmental monitoring, industrial safety, and automotive exhaust control. The exact sensing mechanism can vary depending on the specific metal oxide and the gas being detected. Binary metal oxides are commonly used in gas sensors due to their unique properties that make them sensitive to various gases. These metal oxides typically consist of two different metal elements combined with oxygen. The gas sensing mechanism of MOS based on nature of selected material and also the nature of targeted gas. If the material is n-type MOS and gas is reducing then the resistance of the film is decreased [25, 26]. While if material is p-type MOS and gas is reducing then the resistance of the film is increased as shown in figures 4 (a) and (b) respectively.

![Schematic diagram of (a) n-type and (b) p-type MOS sensing mechanism in presence of reducing gas](image)

Following are the some important gas sensing mechanism of MOS based gas sensors [25-31]:

2.1 **Material Properties**: Metal oxide semiconductors, such as tin dioxide (SnO$_2$), zinc oxide (ZnO), or tungsten oxide (WO$_3$), are typically n-type semiconductors. This means that they have an excess of free electrons in their crystal lattice. In the same way the MOS like copper oxide (CuO), cerium dioxide (CeO$_2$) and Manganese dioxide (MnO$_2$) are p-type semiconductors. This means that they have an excess of free holes in their crystal lattice.

2.2 **Adsorption of gas Molecules**: When a MOS-based gas sensor is exposed to a specific gas, gas molecules adsorb onto the surface of the metal oxide material. The adsorption is typically physisorption or chemisorption, depending on the gas and the surface properties of the oxide.

2.3 **Change in Surface Conductivity**: The adsorbed gas molecules interact with the surface of the metal oxide, leading to a change in the material's electrical conductivity. The exact mechanism can vary depending on the specific metal oxide and the gas involved.

**Chemisorption**: Some gas molecules chemically react with the surface of the metal oxide by donating or accepting electrons, creating charge carriers (electron-hole pairs). This can either increase or decrease the conductivity of the material, depending on the gas and the oxide's properties.

**Physisorption**: For some gases, especially those that do not chemically react with the metal oxide, adsorption leads to changes in the surface's electronic properties, which can also influence the material's conductivity.

2.4 **Measurement of Electrical Changes**: The electrical conductivity of the metal oxide semiconductor is measured using electrodes. Typically, the sensor is part of a Wheatstone bridge circuit or similar setup. Any change in the conductivity of the metal oxide due to gas exposure leads to an imbalance in the bridge, resulting in a measurable electrical signal.

2.5 **Output Signal**: The change in electrical conductivity, and hence the output signal, is proportional to the concentration of the gas being detected. This change can be monitored and calibrated to provide accurate information about the gas concentration.
3. **Impact of doping on gas sensing properties of metal oxide semiconductor**

Doping, the intentional introduction of certain foreign elements or impurities into a metal oxide semiconductor (MOS), can have a significant impact on its gas sensing properties. Doping can be used to enhance the sensitivity, selectivity, and overall performance of MOS gas sensors [32, 33]. Doping affects the gas sensing properties of metal oxide semiconductors as follow-

3.1 **Sensitivity Enhancement:**
Doping can increase the sensitivity of MOS gas sensors. By introducing dopant atoms, the number of charge carriers (electrons or holes) in the semiconductor can be adjusted. This, in turn, affects the material's electrical conductivity. Increased sensitivity allows the sensor to detect lower concentrations of target gases [31].

3.2 **Selectivity Improvement:**
Doping can be used to tailor the selectivity of MOS sensors. Different dopant atoms can alter the surface chemistry and reactivity of the metal oxide, making it more specific to certain gases. This enables the sensor to distinguish between different gases in a mixed environment.

3.3 **Operating Temperature Reduction:**
Some metal oxides require high operating temperatures to function effectively. Doping can lower the optimal operating temperature of a sensor, making it more energy-efficient and suitable for practical applications where high temperatures are undesirable.

3.4 **Stability and Reversibility:**
Doping can improve the stability and reversibility of gas sensors. It can reduce the tendency for the material to undergo undesirable chemical reactions or structural changes when exposed to gases, leading to more reliable and long-lasting sensors.

3.5 **Response and Recovery Times:**
Doping can influence the response and recovery times of MOS gas sensors. It can optimize the kinetics of gas adsorption and desorption processes, allowing for faster and more efficient sensing.

3.6 **Wide Range of Gas Detection:**
Doping can expand the range of gases that a sensor can detect. Different dopants can be used to sensitize the MOS to various gases, making it versatile for multiple applications.

3.7 **Enhanced Electrical Conductivity:**
Some dopants can increase the electrical conductivity of the metal oxide semiconductor, leading to improved signal-to-noise ratios and more robust sensor performance.

3.8 **Reduced Cross-Sensitivity:**
Doping can reduce cross-sensitivity to interfering gases. By tailoring the sensor's response to specific gases, it becomes less prone to interference from other gases present in the environment.

3.9 **Cost and Resource Optimization:**
Doping can sometimes replace or reduce the need for more expensive or less abundant materials, making the sensor fabrication process more cost-effective and sustainable.

The addition of impurity in MOS is play a key role for gas sensing and other applications also. Doping enhanced the performance of prepared films as well as sensor as compare to pure material. Doping also changes the electrical, structural and physiochemical properties of host material [34, 35]. Figure 5 shows the impact of doping on few gas sensing parameters.
**Fig.5:** Gas sensing parameters affected by doping.

**Conclusions:**
Dopant is play very important role in gas sensing mechanism. It is changes the electrical, structural and physiochemical properties of base material. Choice of dopant, its concentration, and the fabrication techniques used can all influence the impact of doping on the gas sensing properties of metal oxide semiconductors. Therefore, careful selection and optimization of doping parameters are crucial to achieving the desired sensor performance for a specific application. The gas sensing properties of binary metal oxides depend on factors such as the specific metal oxides used, their crystal structures, operating temperatures, and the presence of dopants. Additionally, these sensors often rely on changes in electrical conductivity, work function, or other electrical properties when exposed to target gases. Researchers continue to explore and optimize these materials for improved selectivity, sensitivity, and energy efficiency in gas sensor applications across various industries, including environmental monitoring, industrial safety, and healthcare.

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**Conflicts of Interest:**
The author declare no conflict of interest.

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