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SENSING MECHANISM FOR SEMICONDUCTOR GAS SENSOR

P. K. Saraswat, Ph. D.

Associate Professor, Deptt of Physics, Narain College Shikohabad (Firozabad) U.P. -283135

Abstract

Gas monitoring devices are in demand for a rapidly growing range of applications. Metal oxide-based gas sensors have been extensively used for the detection of toxic, pollutant gases, combustible gases, and hydrocarbon vapors. The sensitivity for low concentration and observed response ad recovery times of the reported gas sensors are not satisfactory and it needs further detailed studies. The changes in microstructure influence the sensitivity (response) of the sensor. The response of the sensor drastically changes due to changing the microstructure like grain size. The response of the sensor can be improved also by changing the microstructure and porosity of the semiconductor metal oxide. A finely dispersed small crystallite has a deleterious effect on the temporal stability of the sensor. Environmental humidity is also an important factor influencing the response of the semiconductor metal oxide gas sensors.

Keywords: *Sensitivity, Sensing Mechanism, Doping Material, Physisorption.*

Discussion and Analysis: The basis of operation of most n-type metal oxide semiconductor gas sensors is the variation in resistance of the sensing materials which results due to interaction between oxygen on the oxide and the gas molecules to be sensed. The oxygen will be adsorbed on the surface and acts as electron accepter when the metal oxide semiconductor is exposed to the air. The oxygen ions (O-, O_{-2} or O_2 -) are formed when adsorbed oxygen species will capture electron from the surface. The oxygen ions lead to the formation of a surface depletion layer. Thus, carrier density in the metal oxide semiconductor is decreased, leading to an increase in sensor resistance. The charge transfer process is very important in understanding of gas sensing mechanism as most of the process occurs at the surface of a metal oxide semiconductor. The surface between the metal oxide semiconductor and gas is referred as to free surface or just a surface. It is well known and reported that the change in the surface conductance of the semiconductor is caused by the presence of the gas that perturbed the equilibrium of material at a constant oxygen pressure. The process of the oxygen adsorption at the surface is known to be dependent on temperature. At low temperatures (<150° C), the process of the oxygen adsorption is known as physisorption where the bonding between the surface and the oxygen is by the Vander Waal forces. It involves small binding energy that causes an insignificant change in the electrical properties, where the oxygen is in its molecular form. This state acts as the precursor of the next state. At higher temperatures the oxygen ionic species participate in theinteractions and produce a depletion layer at the metal oxide surface. This process is known as chemisorptions and occurs in the temperature range 200° C to 500° C. In this type of reaction, the binding energy exceeds 0.5 eV. It is well known that the oxygen molecules from the ambient are adsorbed at the surface of the metal oxide, subsequently converted into anions after capturing an electron from the conduction band as represented by the following equations [84-85];

$$O_{2\,(gas)} \leftrightarrow O_{2\,(ads)}$$
$$O_{2\,(ads)} + e^- \leftrightarrow O_2^-{}_{(ads)}$$
$$O_2^-{}_{(ads)} + e^- \leftrightarrow 2O^-$$
$$O^-{}_{(ads)} + e^- \leftrightarrow O^{2-}{}_{(ads)}$$

O2 - is a single ionized oxygen molecule, O-is single ionized oxygen, O2- is double ionized oxygen and e- is a conduction band electron captured from the surface. This explains the high resistance (low conductance) of the metal oxide sensors when the electrons are captured by oxygen that leads to the decrease in carrier concentration of the material.

The presence of reducing gas such as Hydrogen (H2), Methane (CH4), and Ethanol (C2H5OH), etc., near the surface of sensor will result in a reaction between the adsorbed charged oxygen ions and the reducing gases that releases the captured electrons back to the conduction band of the sensor's material. Thus the carrier's concentration is increased and caused the sensor resistance to be reduced. The following equations demonstrate these behaviors;

$$R + O^- \Rightarrow RO + e^-$$
$$R + O^{2-} \Rightarrow RO + 2e^-$$

where

R= Reducing gas. The reduction in the sensor resistance would be proportional to the amount (concentrations) of the target gas. The oxidizing gases such as ozone (O3) and nitrous (NOx) the oxygen from the gas will attract more electrons from the conduction band of the sensor material which results in a reduction in carriers' concentration and thus, increase of the sensor resistance.

Factors Influencing Sensitivity and Selectivity of Semiconductor: The changes in microstructure influence the sensitivity (response) of the sensor. The response of the sensor drastically changes due to changing the microstructure like grain size. For a large grain where D (grain size) >> 2L (thickness of the space charge layer), the conductance is limited by Schottky barrier at grain boundaries (known as grain boundary control). If D=2L, conductance is limited by necks between grains (known as neck control) and if D < 2L, conductance is influenced by every grain (known as grain control). The response of the sensor can be improved also by changing the microstructure and porosity of the semiconductor metal oxide (SMOs). Porous metal oxides with higher surface areas exhibit increased gas response. Another approach to enhance the response is added to some suitable doping material or impurities. The smaller grain size is better for the sensitivity of gas sensors, however, an excessive decrease in grain size decreases structural stability. A finely dispersed small crystallite has a deleterious effect on the temporal stability of the sensor . Environmental humidity is also an important factor influencing the response of the semiconductor metal oxide gas sensors. The response of the metal oxide gas sensors decreases with increase in humidity.

The Sensing Mechanism of Resistive-based Gas Sensors for the Detection of Hydrocarbons: The well-accepted sensing mechanism for the detection of gases by resistive-based gas sensors is the change in the sensor resistance when exposed to the target gases. Resistive-based gas sensors are among the simplest types of gas sensors because the measuring of the resistance measurements of a sensor is simple using a simple instrument.

The general sensing mechanism of MOSs sensor for volatile organic compound (VOCs) gases shows a schematic diagram of the sensing mechanism in n-type and p-type metal oxides in the presence of VOC gases, respectively. When an n-type semiconducting metal oxide is exposed to air, the adsorption of oxygen on the sensor surface will cause the ionization of oxygen molecules in the form of molecular ($O_2{}^{-}{}_{(ads)}$) or atomic ($O^{-}{}_{(ads)}$ or $O^{-2}{}_{(ads)}$) ions, depending on the sensing temperature.

Due to oxygen adsorption, a so-called electron depletion layer with a low concentration of electrons forms on the surface of n-type semiconducting metal oxides, which has a higher resistance than the core region of the metal oxide.

Alternatively, a so-called hole accumulation layer will form on the surfaces of p-type semiconducting metal oxides, which has a lower resistance than the core regions of the metal oxides due to an increase in the number of holes as major carriers. After exposing a gas sensor to VOCs gases viz. benzene, toluene, and xylene (BTX), which all are reducing gas, the gas will be adsorbed on the surface of the sensing layer and react with the oxygen ions on the surface, releasing the electrons that were once bound to oxygen back to the surface of the sensor. The reactions of oxygen adsorption with VOCs gases can be shown by general reactions:

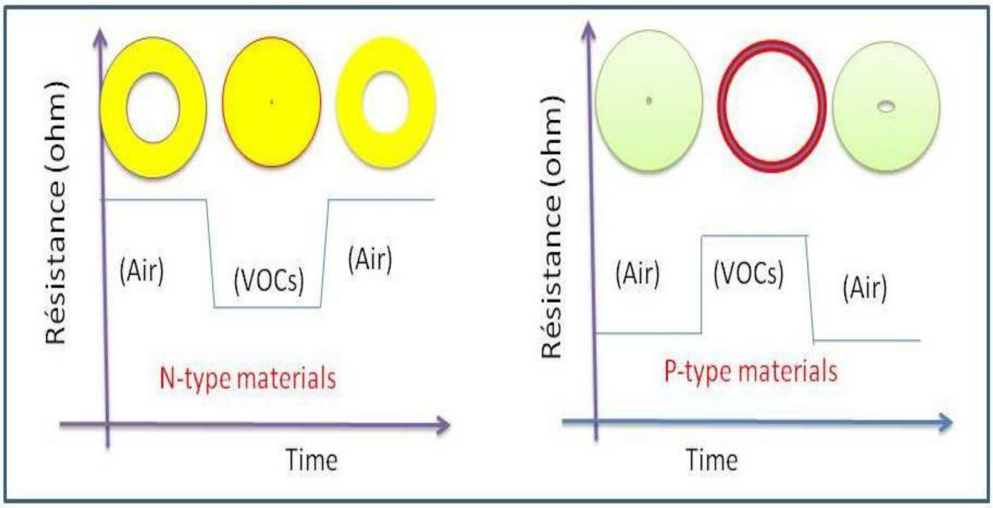
$$\mathbf{CxHy + nO^{-m} \rightarrow xCO2 + yH2O + m.n\ e^{-}}$$

where

For benzene (C_6H_6), toluene (C_7H_8) and xylene (C_8H10) gases, the "x" has a value of 6, 7 and 8, and "y" has values of 6, 8 and 10, respectively.

Accordingly, the width of the electron depletion layer in n-type metal oxides decreases, resulting in a decrease in resistance of the sensor, which contributes to the sensor signal. For p-type metal oxides, the width of the hole accumulation layer decreases due to the combination of the released electrons with holes, resulting in an increase in sensor resistance, which contributes to the sensor signal. This is the general sensing mechanism which is the basic sensing mechanism however; depending on sensing layers the sensing mechanism is more complicated than described.

Various other literatures have been reported on titanium dioxide/tin oxide based gas sensors. They have studied the resistance/conductance response of sensors exposed to a single gas and/or more gases at different concentration, operating temperature, and ambient conditions. The literature survey on oxide gas sensors revealed that the improvement in sensitivity and response time of titanium dioxide sensor depends on so many factors such as doping material (wt%), paste compositions, firing temperature variation, film thickness, crystallite size, grain size, and roughness parameter, etc. Keeping the above-mentioned point in view, an attempt has been made to fabricate a ***CdS-doped Titanium dioxide and ZnO thin/thick film sensor. The structural, optical, electrical, and morphological properties have been studied. The fabricated sensor has been found to be sensitive to various hydrocarbon gases.***



General sensing mechanism of the resistive based sensor in presence of VOCs gas (a) n-type (b) p-type

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