Factors Influencing On Sensitivity of the Metal Oxide Gas Sensors

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Abstract: ***Nanomaterials such as nanorod, nanowire, nanoflakes, nanoflowers and nanoparticle have dominated the research interest in gas sensing application due to their large number of surface sites facilitating surface reactions. So, depending on the surface reaction sensitivity of a gas sensor may vary. So the factors such as chemical components of the composites, microstructure, surface modification, doping, temperature and humidity have great influence on the sensitivity. In this brief review, sensitivity is discussed and formation of hexagonal nanorod is investigated.). Use this document as a template and as an instruction set.***

Keywords: Gas sensor, metal oxide, surface reaction, sensitivity**.**

1. Introduction

One dimensional nanostructure of metal oxides has attracted much attention as a general platform for gas sensing. The detection is done on the basis of measuring the change of conductance, capacitance, resistance and optical characteristics. [1] Researchers have shown the main characteristics of a resistive gas sensor depending on the reaction between the gas and the surface of the sensing layer.[2] This reaction can be influenced by important factors such as properties of seed layer [2] surface area,[3] uniform shape and size distribution,[4] doping, temperature, position of the electrode and heater [5]. The sensitivity of gas sensors relies on these factors. Sensitivity is one of the important parameter which defines the characteristics of the gas sensors in the air (R_a) and the resistance of the gas sensor when target gas is present (R_g). Mathematically sensitivity is defined as,

$S = R_g / R_a$; n-type with oxidizing analyte.

$S = R_a / R_g$; n-type with reducing analyte

Depending on the reaction taking place on the surface of the sensing layer R_a and R_g varies. In this work a brief review of the factors influencing on the sensitivity are studied.

2. Metal Oxide Gas Sensors

Due to the change in conductance and resistance of the metal oxide (MO), CuO, NiO, TiO_2, WO_3, CeO_2, SrO can show gas sensing response. [6] As the electronic structure is the key concern to select metal oxide for sensor, the variety of metal oxides are divided into following categories. [1]

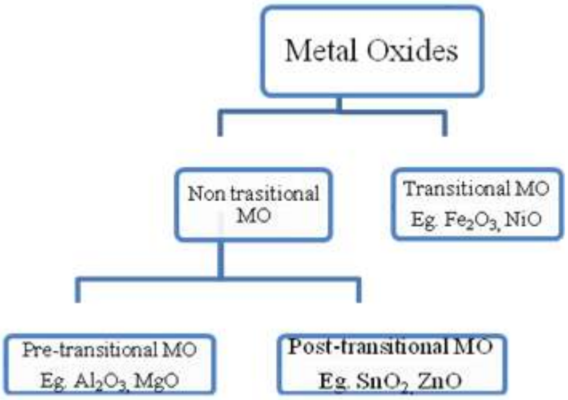

Figure 1: Classification of metal oxides

Pre transition metal oxide semiconductors (MOS) are having large bandgap. So it is not suitable to choose a pre transition MOs because electrons-holes ca not be formed easily. I t is difficult to measure the conductivity or charge in resistance. Mainly due to structural instability transition MOs are not useful for this application. But metal oxides having d^0 and d^{10}electronic structure is potential enough in the field of gas sensing application. Binary transition metal oxides, TiO_2, WO_3 are having d^0 and post transition ZnO, SnO_2 are d^{10} configured.

3. Gas Sensing Mechanism

It is necessary to discuss the principal of operation of a gas sensor. In resistive sensor, electrode is required to measurer the change in resistance on target gas. On exposure to the gas, resistance of the oxide may increase or decrease depending on the type of gas interacting and the dominant charge carrier. Table 1 depicts the sensor responses of n-type material to oxidation or reducing gas. Depending on the MO, a microheater is also needed to achieve the working temperature of sensing layer. Resistance changes because of trapping of electrons at adsorbed molecules and band bending induced by the charged molecule. Upward bending occurs when the negative charges are trapped in these O_2 species and thus a reduced [7] conductivity compared to the flat band situation. As shown in figure 2. [8] O_2 molecules are adsorbed on the surface of the sensing layer; electrons are extracted from the conduction band (E_c) and trap the electrons at the surface in the form of ions. It causes electron – depleted region i.e. space charge layer and band bending. Reverse band bending may occur when reaction of these oxygen species with reducing gases decreases. It results decreased resistance and increased conductivity. O^- is assumed to be a dominant for a specific temperature [9]. Depending on the active metal oxide a specific working temperature is needed to get activated. [10]

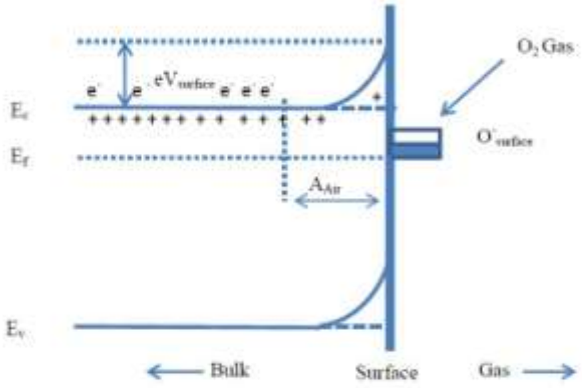

Figure2: Schematic representation of band bending after chemisorbed charged species.

4. Influencing Parameters on Sensing

Temperature is the key factor for adsorption and the reaction of analyte gas. So the metal oxide based gas sensors are also having a heater that permits to work at specific temperature. For an n-type material with a reducing analyte, the value of the sensitivity ($S = R_a / R_g$) is more than 1. In case of n-type material with oxidizing analyte, sensitivity ($S = R_g / R_a$) also becomes more than 1. It becomes reversed when p-type materials are considered. From slope of sensor's calibration curve sensitivity is defined. It is basically the degree of which response proportionately increases with the increment of the concentration of analyte. The response time (t_{res}) and the recovery time (t_{rec}) of gas sensors imply the time taken for resistance to achieve 90% of its steady state value on exposure or removal of the gas respectively. Sensitivity, responsivity, selectivity, response & recovery times, operating temperature are important parameters for a gas sensor. [11] The factors effecting on sensitivity of a gas sensors are analyzed in this paper.

Table 1: Sensing response depending on n-type and p-type materials to reducing and oxidizing gases

Sensor-response behaviour	n-type MOS	p-type MOS	Example of target analyte
Oxidizing gas	Resistance increases	Resistance decreases	O_2, O_3, NOX, CO_2, SO_2
Reducing gas	Resistance decreases	Resistance increases	H_2, H_2S, CO, NH_4, Ethanol, Acetone, CH_4
Dominant-charge carrier	Electrons (e^-)	Holes (h^+)	-

Table 2: Structure architecture nomenclature

Notation	Example	Representation
Hyphen	SnO_2 - ZnO	Mixture of two constituents, randomly distributed
@	SnO_2 @ ZnO @ CuO	A base material with some oxides added over it in some way
Forward slash	SnO_2 / ZnO	Well defined partition between two metal oxides forming by layer

5. Factors on Sensitivity

5.1 Composite Materials

Incorporating two or more metal oxide to form a heterojunction interface can show a drastically change in sensor performance. Table 2 represents three different structure-architecture nomenclatures. [11]

The work on ZnO-CuO [12],SnO_2 – ZnO [13-14],Fe_2O_3 – ZnO [15] have been reported. Combination of MOS with graphene are investigated.[16]Sensing material incorporated with another MOS is found to be more sensitive than individual components. Synergistic effect in this regard is important for future research. It is reported thatto dehydrogenate butanol a combination os SnO_2 – ZnO_2 is more effective than solely from SnO_2 or ZnO_2. $ZnSnO_3$ @ SnO_2nanoflakes have also been reported for enhanced sensing application [17].

N-type gas sensors are mostly used due to several considerations like responsivity, stability in low oxygen environment [18]. These n-type MOSs are often combined in different ways to obtain the effect of P-N junction on sensor performance [19-22]. Fermi level (E_F) is different for different material. After combination of materials electrons start moving from high energy state to lower energy state to achieve equal E_F. This phenomenon is called “Fermi level mediated charge transfer”. This forms depletion layer. Band bending is caused and it results a potential barrier at the interface. Considerable change in sensitivity is reported when ZnO nanowires are decorated with p-type Co_3O_4.[19] Sensor response rapidly changes when Cr_2O_3 is applied on ZnO nanowire [23].

Interface independent complimentary synergistic behavior is an important mechanism for composite material. It happens when two constituents in a composite are each in contact with the analyte serving complementary purpose of each other. It has been investigated as either complimentary decomposition [24] or as spill=over-effect [25].

5.2 Microstructure

It is necessary to fabricate MOS having crystallographic structure and optical morphology. Sensitivity is significantly enhanced with reduced grain size. Geometric consideration involves in sensitivity. Grain size reduction leads to the enhancement of surface area. In smaller grain size particle, nanoparticles are mostly within the depletion area which increases the sensitivity. And active area of reaction becomes more when the surface area is large. It is also significantly enhances the sensor response. For an example SnO_2 based gas sensor response drastically changes when the particle size becomes smaller than 10 nm [26].

5.3 Control Synthesis of Nano or microsized Particle

The gas sensing properties rely not only on their composition but also their structure, shape, size, distribution. Depending on the metal oxide semiconductor specific crystallographic orientation gives better result in sensitivity. In ZnO, (002) crystallographic orientation shows better sensitivity [27]. Beside crystallographic orientation high surface to volume ratio is also very important to achieve better sensitivity. High surface to volume ratio is not only depending on the grain size but also in highly ordered pore structure. ZnO is synthesized and samples are characterized by scanning electron microscope (SEM) which is shown in figure 3 and figure 4. Modification of surface morphology is done by chemical treatment and varying annealing temperature. Figure 4 confirms the formation of hexagonal shape ZnO. Hexagonal structure with high surface to volume ratio results goodsensitivity.

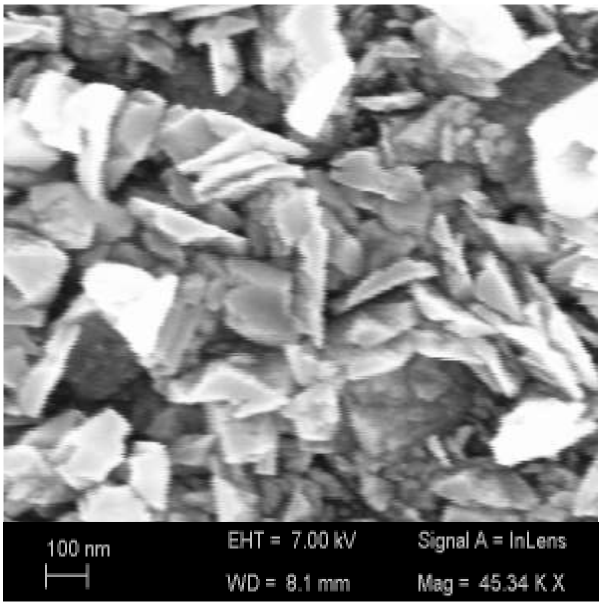

Figure 3: SEM image of ZnO before chemical treatment.

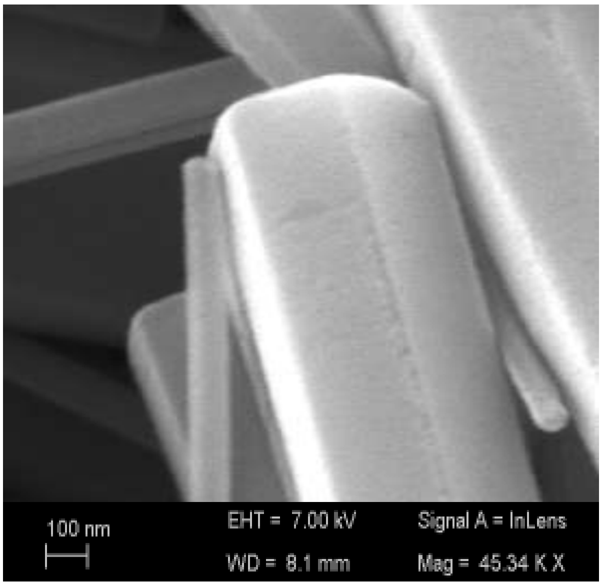

Figure 4: SEM image of Hexagonal ZnOnanorod

5.4 Doping by Nobel Material

Conductivity is measured by the efficiency of catalytic reactions with the target gas on surface of the sensing material. So, the catalytic activity is also a major issue to increase the sensor performance. Most of the pure metal oxides are comparatively least active than doped one [28]. Doping can be done by sol gel process or by thermal evaporation or sputtering. Sometimes mixture of noble materials and MOSs are required or only surface modification. Second phase nanoparticle such as Pd, Ag, Au and Pt are effectively used as a noble particle applied to host metal oxide with enhanced sensitivity [29-34]. Nobel metal nanoparticle behaves like a catalyst and reduces the activation energy resulting the improved molecular dissociation and reaction. [35] Pd-functionalized SnO_2 is reported to be enhanced performance [36]. PdO-decorated ZnO nanostructure is investigated and better sensitivity is also reported [37].

5.5 Temperature and Humidity

Temperature is also a major factor for the metal oxide gas sensors. The gas sensor responses increase and reach their maximums at a certain temperature, and then decreased rapidly with increasing the temperature. This is a common tendency seen in many reports [38-41]. In ZnO based sensor the maximum response is found at 200-300^{0}C.[41-42]. Sensitivity decreases below or above the specific temperature.

Humidity is an important issue in gas sensor performance. Humidity sometimes lowers the sensitivity. Baseline resistance of the gas sensor decreases when the reaction between the surface oxygen and the water molecules occurs, [42]. So, the sensitivity is decreased. Adsorption of water molecules causes less chemisorption of oxygen species on the ZnO surface as surface area gets decreased. And it effects on sensitivity. Water molecules are basically the barriers against target gas adsorption. So response recovery times increases and sensitivity decreases.

6. Conclusion

In brief, sensing properties mainly rely on the surface reaction. Some specific metal oxide and their composite materials show better sensing response. Structure of the nanoparticles is also a great concern. High surface area is important to get highly – dispersed catalyst particles. High surface to volume ratio can accommodate large and target analytes. It is investigated that hexagonal structural morphology can be obtained by doing chemical treatment and varying annealing temperature. Doping of nobel metal additives with high catalytic activity may enhance the sensitivity because of “spillover effect”. Crystal growth at specific orientation has major effect on sensitivity. On other hand temperature and humidity are also playing an important role in sensitivity. Humidity drastically lowers the sensitivity. But this problem can be ignored by incorporating temperature from microheater.

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