Efficiency Improvement in Metal Oxide Gas Sensor Relays

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Abstract

Semiconductor metal oxides are widely used for different applications in different fields. In this review, we discuss various metal oxides like ZnO, SnO_2, TiO_2, WO_3 and CuO that has different synthesis process where different characterizations are adopted. It also shows the variations and effect on different parameters of sensor device such as sensitivity, response and recovery time.

Keywords: - *Metal Oxides, Semiconductor, Characterization, Sensor, Synthesis.*

INTRODUCTION

Semiconductor Metal Oxides are widely explored chemiresistive gas sensors [1]. Mostly gas sensors can be of electrochemical or metal-oxide semiconductors in thick-film or in thin-film [2]. Metal oxides are favorable for usage in different aspects in domestic, industrial and commercial applications [3]. Applications of gas sensors are seen in wide aspect like monitoring the air quality, detection of toxic and harmful gases, medical field etc. [4].

Different reviews conclude that the gas sensing process strongly depends on the sensitivity of the material that has an influence on the chemical components, surface-modification and microstructures of sensing layers, temperature and humidity [1].

Metal oxide gas sensors must have a large surface area so as much target gas as possible can be absorbed in order for better measurement of the gas response [3].

Semiconductor metal oxide gas sensors are selectively advantageous in the detection of toxic gases over others due to low cost, small size, measurement simplicity, portability, sensitivity, durability, ease of fabrication, the simple working principle and low detection limits [5]. They are useful for the detection of combustible, reducing or oxidizing gases by means of conductivemeasurements [1]. They also help for the detection of harmful gases like CH_4, C_3H_8, H_2, CO, H_2S, formaldehyde, ethanol, methanol, butanol etc. [6].

MATERIAL SYNTHESIS

According to Lin et al., TiO_2 nanotubes were fabricated for the detection of formaldehyde at room temperature [7]. They were synthesized by the electrochemical anodization process. Initially, the titanium sheets were cleaned with acetone, ethanol and deionized water for about 10 mins each. In the process, Ti was used as working electrodes and stainless steel as the counter electrode. The sample was then anodized in a mixture of 0.27 M NH4F with deionized water and glycerol and held at 30V for 3 hrs [7]. Similarly, Xu et al. investigated another metal oxide like ZnO nanoparticle that was synthesized by chemical precipitation method [6]. Firstly ammonia was diluted of 1.5 mol/L in the presence of deionized water. The resultant was then mixed with Zinc acetate[Zn(CH3COO)2] and deionized water solution. The precipitate was held for about 1 hr, then processed with filtering, washing, drying at 378K and finally sintering at 873K, and lastly left for cooling [6]. Again Wang et al. made an attempt on analysis of ZnO nanorods by the hydrothermal process at room temperature to detect ethanol [8]. In this process, cetyltrimethylammonium bromide and sodium hydroxide were dissolved for 20ml of distilled water. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was again dissolved for 20ml of distilled water to form $Zn(NO_3)_2$ and added to the previous solution, which was heated for 15 hrs. at 90°C. White solid residues were then removed from the solution and then washed with distilled water repeatedly and left to dry at about 80°C [8].

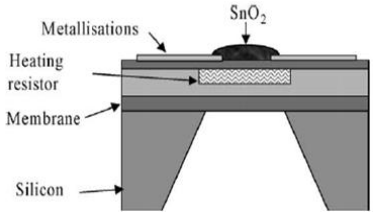

Fig. 1: Typical SnO_2 gas sensor [2]

Another such metal oxide SnO_2 was studied by Ménini et al. for the sensing of CO [2]. The gas sensor that has been developed has micro hotplate architecture, as shown in figure 1. The dielectric membrane (2µm thickness) helps to support heater of 600 µm × 430µm. One set of platinum electrode pair was connected to heating resistance, while the other pair helps to receive the signal. The optimum temperature of the heater has been observed to be around 500°C with 100mW power consumption. The heater helps in the oxidation of SnO_2 at 500°C with optimized sensitivity and selectivity [2].

MATERIAL CHARACTERIZATION

Semiconductor metal oxides can be characterized in different ways, such as Field Emission Scanning Electron Microscopy (FESEM), Photoluminescence spectroscopy (PL spectrum), X-ray photoelectron spectroscopy (XRD), Scanning Electronic Microscopy (SEM), Raman Spectroscopy etc. Lin et al. studied TiO_2 nanotubes by X-ray photoelectron spectroscopy at as-fabricated, 400°C and 500°C [7]. The as-fabricate sample was amorphous in nature and retained that phase until 300°C. In figure 2, the peaks are observed for the sample at 400°C and 500°C in the crystalline phase. As the temperature increases, the sample crystallized into two phases. At lower temperature, anatase was observed while at higher rutile can be seen[7]. WO_3 is another such metal oxide that has been characterized by XRD in order to study the crystalline nature of porous and sputtered material.

Zeng et al. investigated porous WO_3 and observed lattice parameters to be a = 7.30Å, b = 7.53Å, c = 7.68Å and β = 90.9° while for sputtered WO_3a = 7.297Å, b = 7.539Å, c = 7.688Å, and β = 90.91°. It has also been observed that the strongest peak appears at 23.14° for porous WO_3 whereas 25.58° for sputtered WO_3. The particle size thus strongly determines the sensitivity of the sensor [9]. Xu et al. studied XRD and TEM of nanosized ZnO powder in the range of 20°-70° with scanning step size 0.03° s^{-1} [6]. Similarly, XRD and PL spectrum analysis was made on ZnO nanowire by Ahn et al. [10].PL spectrum was received by excitation of 325 nm He-Cd laser at low temperature. The analysis thus shows that major peaks were observed at wavelength λ = 380nm and λ = 490 nm [10]. Again XRD analysis w made on ZnO nanorods for the range of 2θ = 20° to 80°. SEM image at 15 KV and TEM image at 200 KV [8].

Wang et al. thus concluded that the peaks observed from XRD image are identical with Bragg reflections of the standard hexagonal wurtzite ZnO structure [8]. SnO_2 film characterized by XRD pattern showed tetragonal structure with a = 4.7382 Å and c = 3.1871 Å. The material was studied by Liu et al. for ethanol detection at 50°C and in the temperature range of 200-500°C [4].

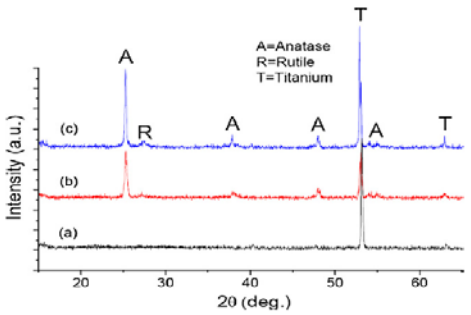

Fig. 2: TiO_2 nanotube arrays characterized by XRD at different temperatures (a) as-fabricated (b) 400°C and (c) 500°C. [7]

SENSOR STUDY

The n-type WO_3 metal oxide semiconductor has a bandgap of 2.7 eV are studied for sensing material [11]. Chen et al. reported that single-crystalline WO_3 nanoplates were synthesized by a topochemical approach with high sensitivity towards alcohols [12]. The sensitivity of WO_3 for methanol, ethanol, and butanol was found to be 33 at 300 ppm, 70 at 200 ppm and 31 at 2 ppm at 300°C, respectively. The response and recovery times found to be 15s for all the gases. When optimum temperature increases both sensitivity and response time decrease[12].

Vallejos et al. has studied flexible gas sensor devices of highly crystalline WO_3 nanostructure, functionalized with gold or platinum nanoparticles that showed better sensitivity towards Volatile Organic Compounds (VOCs) [13]. The sensitivity of the device for ethanol is 1.3 for Au/W and 6.7 for Pt/W with ethanol concentrations of 0.2, 0.1 and 0.05% at 220°C. The response time for Au/W and Pt/W were 217s and 30s, respectively. The recovery time was analyzed for Au/W as 400s and 970s for Pt/W[13].

Khot et al. reported that CuO used for sensing NO_2 gas synthesized by spray pyrolysis method could detect upto5ppm of gas [14]. The sensitivity of

CuO was maximum at 200°C with 56% for CuO concentration 0.15. The recovery time and response time were followed to be 20.57s and 3.92 for 100ppm of NO_2 [14].

Molavi et al. had reported that aluminium doped CuO nanostructure has a better response than pure CuO nanostructures [15]. The maximum response of Al/CuOwas67% at 150°C to 800 ppm CO and that of pure CuO was 48% at 120°C. Response time of both CuO and Al/CuO sensors lies between few seconds and recovery times up to 1 minute[15].

SENSING MECHANISM

The working principle of metal oxide gas sensor depends on the electrical conductivity or resistivity change of thin films when exposed to target gas. The gas molecules present in the ambient atmosphere are either oxidizing or reducing type gases. These gases either donate or accept the electric charges[11]. The sensing mechanism of the gas sensor is shown in figure 3.

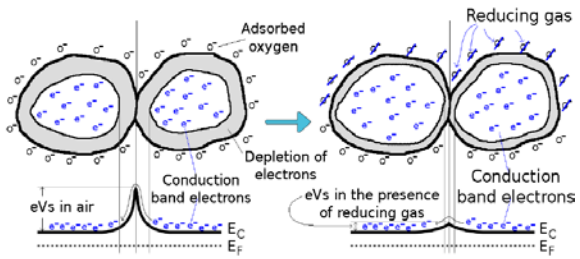

Fig. 3: Gas sensing mechanism of metal oxide [16]

The oxygen molecules interact with the metal oxide surface as oxygen anions from the depletion layer around the grains and thereby increases potential barrier. When target gas molecules interact with the metal oxide grains, oxygen anions is desorbed, which makes the majority carrier concentration change inside the oxide layer, which thereby changes conductivity[16].

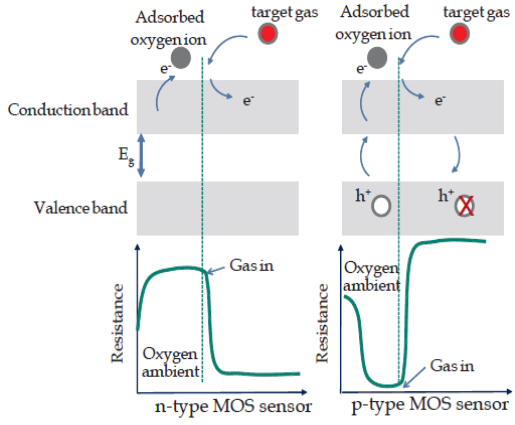

Fig. 4: The graphs show the effect of resistivity on PMOS and NMOS when exposed to reducing gas [17]

The operating temperature is an important factor that enhances the adsorption of gas molecules [11].

The resistance of n-type metal oxide thin film increases when the target gases are oxidizing and decrease by reducing gas, whereas the resistance of p-type material decrease by oxidizing gases and increase upon exposure to reducing gas. When there is reducing gas in the ambient of gas sensor, the electrons taken by the oxygen atom is released after reaction with reducing gas which can be seen from figure 4 [17]. The humidity plays a great role in the sensing of metal oxide sensor [11]. The efficiency can be improved for metal oxide gas sensors as follows.

A. Doping of Metal Oxide

Additives like Pd, Pt, Au, Ag and Cu greatly enhance the sensing capabilities by increasing interaction between target gas and metal oxide surface with catalytic effect [16].

B. Grain Size

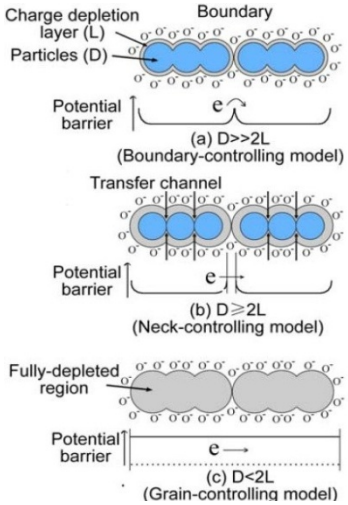

Fig. 5: Schematic model showing the relation of grain size (D) and the width of the space-charge layer (L) affecting sensitivity of metaloxide gas sensors: (a) D >>2L; (b) D ≥ 2L; (c) D < 2L [19].

The gas-sensing performance can be increased by decreasing the size of the grain (D). As shown in fig. 3, the sensing materials are in the form of partially sintered grains connected by necks [18]. The relationship between the grain size (D) and the width of the space-charge layer (L) can be as follows, as shown in figure 5.

a) D>>2L: In this case, large gains are unaffected by gas-solid interaction; hence conductivity and sensing are controlled by grain boundary barriers [18].

b) D ≥ 2L: Here, the depletion layer constricts the conduction channel. The conductivity depends on grain boundary, while a decrease in grain size increases sensitivity.

c) D < 2L: In this case higher response is obtained. The absence of a conduction channel leads to an almost flat energy band with negligible grain boundary for carrier transport; therefore sensing mechanism is controlled by grain [19].

C. Gas Diffusion

Gas sensing can be improved by enhancing the target gas diffusion on sensing material that can be of two kinds. The interaction of target gas takes place only on the surface of denser nanostructure, whereas in the porous nanostructure, inner interaction with gain takes place and hence more gas molecules diffuse [18].

D. Surface Defects

The performance of the gas sensor can be improved by surface defects which can be achieved by calcination below the temperature of 400°C. The ZnO shows the maximum response for acetone gas at 200°C. Surface defects lead to more adsorption of oxygen molecules at the surface when target gas interacts with metal oxide surface. As a result, more electrons will be released, which leads to a better response [18]

E. Effect of the heterojuction

Heterojunctions interface two dissimilar types of semiconductor metal oxide. It has a depletion layer at the interface after an exchange of its carriers. There are two way in which heterojunction improves the sensitivity, one is p-n or n-p junction, and the other is p-p or n-n junction. The p-n or n-p junction acts as a diode with some potential barrier. The ZnO/Co_3O_4 heterostructures have improved ethanol sensing performance where ZnO is n-type and Co3O4 is p-type. When oxygen molecules are adsorbed on the surface, the electron density of n-type material is decreased, and the hole density of p-type material increased. After the interaction with ethanol, the electron density of ZnO increases, whereas Co_3O_4 decreases lead to the flow of the carriers and hence changes resistance. In the case of n-n or p-p junction, an accumulation layer is formed due to the flow of carriers from high fermi level to low fermi level. The accumulation layer is depleted by oxygen molecules and then desorbed by target gas, leading to a change in sensitivity of the sensor [18].

F. Thin film based sensor

The grain size of a crystal has a vital role in sensing. The decrease in size of crystal grain increases the surface to volume ratio, carrier concentration and enhanced catalytic activity that facilitates its interaction with a larger number of gas molecules. Thin-film of nanostructured metal oxide grown has been seen to have a smaller grain size [11].

CONCLUSION

Different metal oxides like ZnO, SnO_2, TiO_2, WO_3 and CuO gas sensors have been studied in this review for the detection of various gases. The paper survey revealed the different factors for efficiency enhancement of the gas sensor. Subsequently, the sensing mechanism of metal oxide gas sensor has been described to understand the requirement of gas sensor to detect toxic gases. Some other factors which affect the sensitivity of metal oxide gas sensor have also been described. These are grain size, doping with a suitable dopant, effect of surface defects, gas diffusion, effects of heterojunction and thin film-based gas sensor.

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Not applicable

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