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The Factors Affecting on the Gas Sensing: Review

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Abstract:

In this review, we discussed the impact of oxygen vacancy, doping, film thickness, annealing temperature, and grain size on the gas sensing. One of the most common defects in thin films is oxygen vacancies, whose concentration varies based on the growth time and the microstructure of the synthesis films. The vacancies of oxygen considered centers for the accumulation of charge carriers, which reducing their losses resulting from recombination and contributes the increasing the life time of photogenerated charge. In addition, the oxygen vacant sites act as active adsorption centers, increasing the amount of chemisorbed oxygen species (O_2^-,O^-) which pull electrons from the conduction band and lead to the creation of a surface depletion layer. Silver atoms on the WO3 sensor surface enhance oxygen adsorbed, thus increasing the chemically adsorbed species such as O^(2-), therefore Ag doping of the WO3 layer successfully improves NO sensitivity. A thicker layer contains more pores and clusters than a thinner layer. In this case, even reactant gas is depleted oxygen and fresh oxygen are introduced, the length of the delay time required for the oxygen to penetrate the thick layer results in slow reabsorption of oxygen ions. Increasing the surface roughness contributes to providing a large surface area, which allows a greater number gas molecules to interact with the surface of film. The number of cracks in the thin film's material is related to an increase in resistance, which depends on the layer thickness and applied deformation. Although the cracks may be pathway for gas entrapment, they are also very likely to cause an electrical breakdown that in this area. Annealing in air leads to increased oxygen vacancies generation which enhances gas sensitivity. The grain size has a significant effect on gas sensor based on n-type semiconductor like tin oxide, where electrons pass through potential energy barriers. The number of these barriers, which form at the grain boundaries, decreases as grain size increases.

Keywords: Thin Film, Oxygen Vacancy, Grain Size, Annealing Temperature, Thickness.

Introduction

The mechanism of a gas sensor operating depends on the magnitude of the change that occurs in the conductivity of the semiconductors as results of the interaction with the gas sensor and the gases present in the air. Gas sensing mechanisms assume that oxygen adsorption on the oxide surface, leads to a depletion of electron density, causing decrease in the conductivity of materials. The target gas molecules react with oxygen adsorbed on the surface of the semiconductor gas sensor, causing a reverse transfer of charge [1]. The performance of thin film sensor like sensitivity, response time and recovery time are strongly influenced by the film thickness, shape and film structure [2]. Illuminating the surface of the sensor causes an increase in active sites and enhances the separation of electrons and holes, which leads to reduction in the sensor working temperature and an improvement in sensitivity. Moreover, reducing the band gap contributes to lowering the energy barrier for the transfer of photogenerated electrons, thereby increasing the efficiency of electron-hole separation. Increasing the temperature level in metal -oxide semiconductors represent a practical approach to reducing the band gap [3]. This strategy not only increase in the amount of oxygen adsorbed on the film surface, but also leads to enhances the efficiency of electron - hole separation. The presence of active species on the film surface, defects, and impurities can further improve the performance of thin films sensors. Doping is crucial of modifies the electronic structure, formation of oxygen vacancies materials and band gap energy of metal oxide. Other studies have shown that adding metallic impurities to an oxide matrix in a thin layer increases the layer's sensitivity to certain gases [4]. Particle size is determining the factor for the basic operational properties of sensor, such as response rate and response speed [5]. Currently, reducing particle size is one of the basic means used to improve the response of gas sensors made from solid metal oxides. However, other studies have shown that particle size also affects the sensor's sensitivity to atmospheric humidity [6].

Materials and Methods

This article reviews research and analyzes results related to thin film semiconductor gas sensor, focusing on factors affecting their performance, including oxygen vacancies, doping thickness, annealing temperature and grain size. Studies on these factors were compiled from reputable databases such as Scopus, Science direct and Google scholar.

factors affecting sensitivity

Oxygen vacancies

S. Pati, et al [7]. Study effect oxygen vacancies on gas sensitivity, demonstrating that the one of the most common point defects in thin film is oxygen vacancies. The concentration of these vacancies varies depending on the film microstructure and growth duration. Therefore, the vacancy concentration has a substantial effect on the sensor response properties. These lattice vacant will behaves like sites that are active for the chemisorption of oxygen present in the air during the gas sensor exposure to it. The greater the number of this lattice vacant chemisorption of oxygen, the result is the reaction of many reducing gas molecules (such as CO), which in turn leads to an improvement in the sensor response. This explains why the response rate increases with increasing growth time (which increases film thickness as well as the density of point defects). As the concentration of point defects decreases, the response rate also decreases in this film.

P-X. Wu, et al [8]. Reported the enriched oxygen vacancies in $SnO_{2-x,}$ were the indicates that sensing mechanism can be explained as follow: first, the vacancies of oxygen considered centers for the accumulation of charge carriers, which reducing their losses resulting from recombination and contributes the increasing the life time of photogenerated charge. Secondly, a surface depletion layer is formed due to the trapping of electrons from conduction band by oxygen vacant sites, which in turn increases the density of chemically adsorbed oxygen species. Increasing the proportion of oxygen vacant in thin layer of tin oxide (SnO_{2x}) reduces the energy gap from 3.32ev to 2,83ev, enabling it to be activated by visible light to sense NO_2 at room temperature. The improved performance of sensor (under 450nm irradiation) is due to the synergistic effect of oxygen vacant that enhance the surface

adsorption and narrowing of the band gap enhance the separation of photogenerated charge.

J. Lee, et al [9]. Reported accurate regulation of the oxygen vacancies for extermely high sensing response of aceton. Figure 1 illustrates a possible mechanism for the detection of acetone using pure zinc oxide (ZnO) nanoparticles and oxygen vacant ZnO nanoparticles, based on surface chemistry characterization results. The sensing mechanism based on the magnitude of change in the electrical resistance of ZnO. Upon exposure of ZnO nanoparticles to the surrounding air, adsorption and desorption processes of gas molecules occur on the material of sensor. The oxygen molecules adsorbed on the surface of the gas sensor trap electrons from the conduction band of ZnO figure 1 a. A temperature 400℃ in an air atmosphere is regarded as the optimal operating temperature, where oxygen ions O^{2-} form on the ZnO surface figure 1a. various of oxygen ions are also formed including O_2^-, O^-, O^{2-} depending on operating temperature. Upon exposure of the sample to acetone gas (CH_3COCH_3), many numbers of electrons are released as a result of the interaction between gas molecules with the adsorbed oxygen ions (O^{2-})on the sensor surface, returning to the conduction band of ZnO figure 1a. Subsequently, decrease in the depletion layer thickness lead to reduction in resistance figure 1a. Oxygen vacancies act as oxygen ion acceptors in the air at high temperature. Various types of oxygen ions are absorbed, resulting in a thicker depletion layer figure 1b. In sample containing oxygen vacant, the ZnO nanoparticle resistance in air higher compared to untreated sample. After exposure to acetone gas molecules, the sensor reacts with a larger number of oxygen ions species, leading to siginficant decrease in resistance. Therefore, the sample containing oxygen vacant exhibits a higher response to acetone gas.

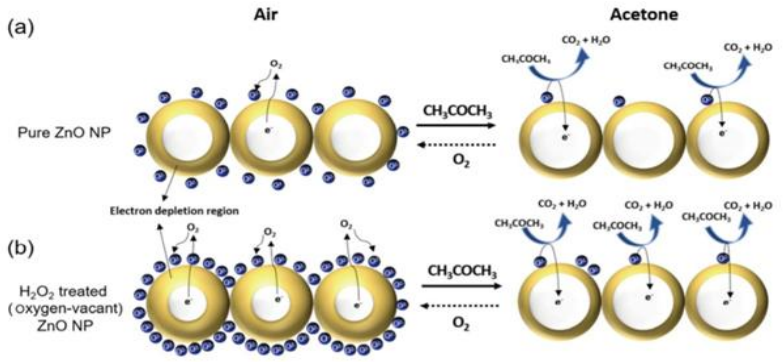

Figure 1. Schematic diagram of sensing mechanism for (a) commercial ZnO nanoparticle (b) H_2O_2 treated/annealed ZnO nanoparticle in air and acetone [9].

K. Ganesan et al [10]. Analysis of the effect of oxygen vacancies on the gas sensor performance. The surface of the nanoparticles acquires p-type semiconductor characteristics, with the formation of an inversion layer due to the increased concentration of oxygen vacant, when WO_{3-x} gas sensor is exposed to ambient air at room temperature, the concentration of oxygen vacant increases, resulting in energy band bending and the presence of p-type inversion layer in the WO_{3-x} nanostructure as shown in figure 2a. When (NH_3) gas reacts with surface material of WO_{3-x} nanoparticle injects more electrons into it. Consequently, at low temperatures below 100℃, the surface p-type inversion layer disappears due to the injection electrons compensate for near – surface holes, and the surface becomes a electrons-depletion region, accompnied by a decrease in the surface barrier potential as shown in figure 2b. The resistance of sensor increases when (NO_2) gas is detection process, as the surface behaves like p-type semiconuctor when exposed to the analyzing gases. This behavior is attributed to the change in the type of charge carriers between the n-type and p-type. In addition, transition occur in the WO_{3-x} nanostructure depending on the concentration of oxygen vacancies during temperature dependent heating and cooling cycles. The nanostructure transition from semiconductor to insulator or vice versa within a temperature range of 100 ℃ to 212 ℃ . The transition temperature decreased with increasing concentration of oxygen vacancies in the WO_{3-x} nanostructure. The gas sensing and the transformation of semiconductor into an insulator or vice versa be is associated with the presence of oxygen vacancies in these materially. The high oxygen vacancies and porous nanostructure with thickness which do not exceed a few nanometers, play a role in unusually distinctive response.

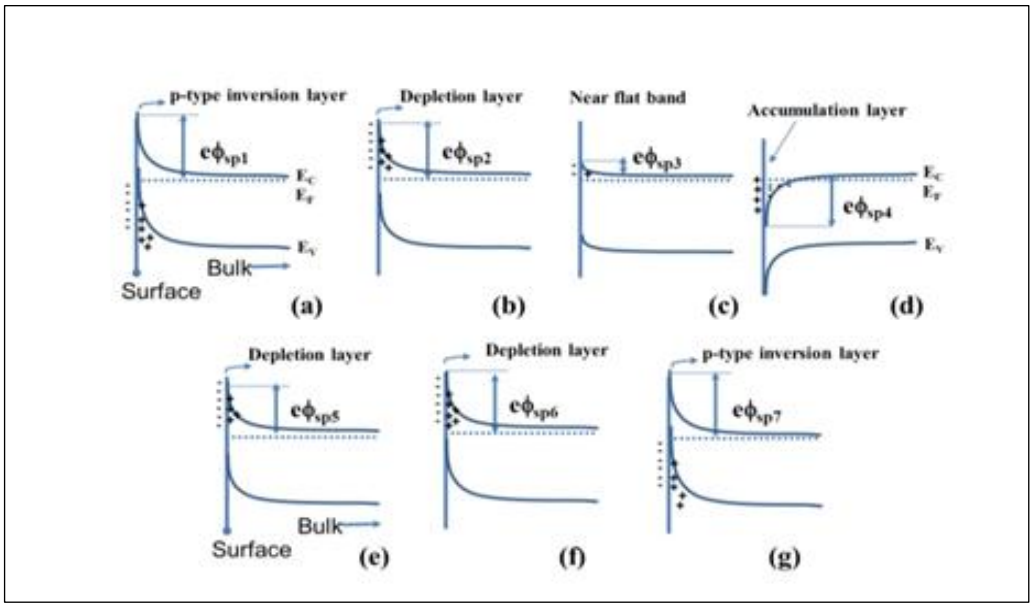

Figure 2. The diagram illustrating the energy band of an n-type WO_3 semiconductor [10].

H. Li, et al [11]. A porous WO_3 thin film characterized by high concentration of oxygen vacancies was fabricated by sputter deposition. Analysis result of XPS indicated that different annealing temperature significantly affects then oxygen vacancies content in WO_3 films. The oxygen vacancies content in WO_3 was 20.1%, 16.8% and 14.8% at annealing temperature of 400℃, 600℃ and 800℃ for 3h respectively. This can be attributed to the fact that annealing at low temperature led to week oxidation, this resulted in lower crystallinity of the formed thin films due to the reduced of grain growth. This reinforces the idea that low temperature annealing is conducive to the creation of oxygen vacancies, which are essential to the process of gas detection. These oxygen vacancies not only act as active sites, but also play a significant role in electron transport within material. Therefore, annealing at 400℃ increased the concentration of the high oxygen vacancies in WO_3, which in turn enhance the response of the gas sensor.

P. Zhou, et al [12]. Alternative description of the self-consistent electronic change employed by oxygen vacancies as well as certain types of ionosorbed oxygen species, it has been assumed to be present in for n-type metal oxide semiconductor. But unlike n-type materials, it is completely different, the oxygen vacancies are often located “deep” in band gab. Therefore, these electrons resulting from the formation oxygen vacancies do not ionize into free electrons, but remain captured at the vacancies. Due to the relatively large number of holes (main charge carriers) in p-type material, it is expected that it will be thermodynamically preferable of electrons captured in oxygen vacancies (inside the band gap) for recombination with valance band holes. The concentration of primary charge carriers in a p-type materials decreases as a result of oxygen vacancies formation. Thus, leading to an increase in resistance (decrease in conductivity) as the concentration of oxygen vacancies increase. Therefore, under reduction condition, concentration of holes is expected to decrease, leading to increasing in the resistance of material surface, oxidation process of the target gas leads to the concentration of oxygen vacancies to rise of the sensing material, resulting in hole annihilates as shown in figure 3, and causing increased resistance. Direct contact with air will cause the surface to re-oxide, which will reduce its concentration oxygen vacancies.

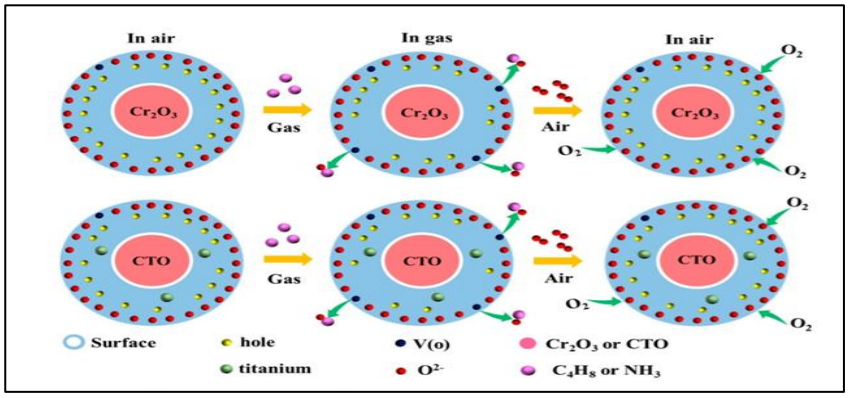

Figure 3. Diagram illustrating the sensing reaction mechanism of thin films of Cr_2O_3 and CTO when exposed NH_3 or C_4H_8 [12].

Doping

A. **Kilic, et al [13].** Reported the CH_3COCH_3 sensor performance of silver-doped titanium dioxide nanorods. They utilized a seed-based hydrothermal treatment method to synthesis the titanium dioxide nanorods, and then loaded with Ag. Ag was deposited onto titanium dioxide (TiO_2) nanoparticles by thermal evaporation of metallic silver for different time 30, 45, and 90s. The researches demonstrated that the increased in the CH_3COCH_3 detection sensitivity of the Ag-doped TiO_2 sensor (45s) was result of the catalysis performance of the Ag. In fact, silver loaded enhanced the number of available surface sites for adsorption on the TiO_2 an increased the rate of electron transfer between CH_3COCH_3 molecules and surface of the titanium dioxide. In a CH_3COCH_3 atmosphere, the bonds between CH_3COCH_3 molecules are readily broken by Ag, promoting the activity of these molecules to react rapidly with chemisorptively adsorbed oxygen species. Furthermore, the deposition of Ag nanoparticles onto TiO_2 nanorods stabilizes the fermi level of TiO_2 because of electron movement from TiO_2 to Ag, thus improving the sensor response to CH_3COCH_3. The reduced CH_3COCH_3 response (90s) is related to the formation of large Ag aggregates on the TiO_2 surface, which hindered oxygen diffusion within TiO_2 and reduced the catalysis performance of Ag.

E. Espid and F. Taghipour [14]. The detection properties of nitrogen dioxide (NO_2) gas were described using Ag- loaded, oval-shaped ZnO nanoparticles, that were manufactured via simple coprecipitation technique, under ultraviolet illumination. Upon irradiation of the sensor surface with photons from an UV-emitting diode, some electrons are jumped from the valence band to the conduction band, resulting in holes appearing in the valence band. The electron-hole pair generated by the Uv illumination of the Ag -doped ZnO sensor during exposure to NO_2 gas enhance oxygen molecules adsorb directly onto the surface as shown in figure 4. In an atmosphere of air, excited electrons react with adsorbed oxygen in its ionic form onto the surface of sensor. This leads to minor increase in resistance of sensor. In an atmosphere of NO_2, oxygen ions react with directly adsorbed gas molecules on the surface of sensor via electron acceptors or chemically adsorbed. Under the influence of continuous ultraviolet radiation, the accelerated photons removed NO_2 molecules from the sensor surface. The significant improvement in NO_2 detection performance using elliptic ZnO nanoparticles after Ag loaded is as a result of the synergistic effects of the semiconductor compound and Ag. Furthermore, the improved performance of sensor with doped of Ag was associated with an increased electron utilization rate and reduce electron and hole recombination rate, resulting from electron trapping in Ag nanoparticles during excited electrons. In the same way, the amount of adsorption was related to the number of oxygen vacancies that are unoccupied were formed due to the difference in charge between the Ag and Zn ions, indicating the creation of more active sites for adsorption, leading to an enhanced sensor response.

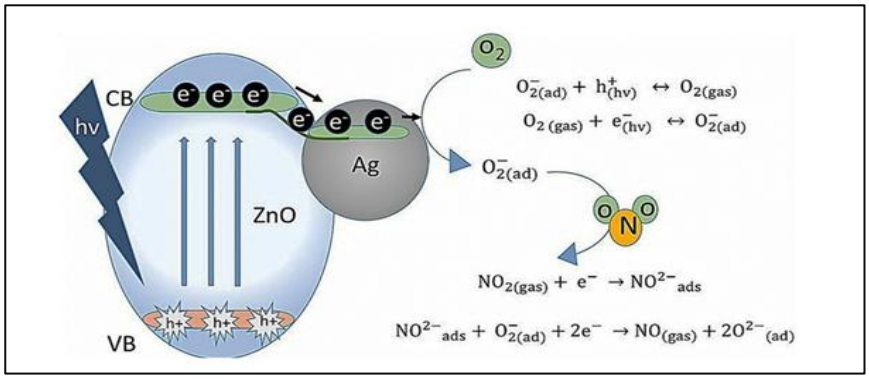

Figure 4. Enhancing NO_2 gas sensing performance using Ag -doped ZnO nanoparticle ellipsoids [7].

S. Tekin [15]. Study the effect of Zn- loaded CuO on sensor response. Since (CuO) is a p-type semiconductor and zinc oxide (ZnO) is an n-type semiconductor, doping copper oxide with zinc (Zn) forms p-n heterojunction structure. As a result of this combined structure, and increase in current conductivity is observed. The hole density in p-type and the electron density in n-type semiconductors are both high, and their fermi energy levels differ. Therefore, when these two structures are brough close to each other at the atomic level, electrons flow between them. This leads to a bending of the energy band configuration for n-type and p-type semiconductors when they are combined for this reason, an increased response is observed in Zn- loaded CuO compared to undoped copper oxide thin film. However, a decrease was observed after the doping rate exceeded a certain limit, and a doping rate of 1% was determined to be the optimal doping rate in this study.

A. Wisitsoraat, et al [16]. Study the effect carbon-doping on sensor performance of molybdenum oxide, we are observed that the electrical resistance of sensor reduces by an order of magnitude upon the addition of carbon, it is clear that adding carbon to reaction deposited molybdenum oxide films causes considerable improvement in the sensing toward ethanol. Furthermore, the increase ethanol sensitivity is similar to the variation in resistance. The sensitivity of ethanol increases by an order of magnitude as result of the addition of carbon. The doping of carbon with molybdenum oxide thin films exhibits an ideal sensitivity to acetone of higher than 30 at a low concentration of ethanol 500ppm with operating temperature of 350℃. Structural analysis indicates that the observed result is mainly due to doped of carbon rather than changes in shape or structure.

Q. Tang, et al. [17]. The effect of adding platinum on sensor performance can be traced back to be phenomenon of diffusion. Various types of chemically adsorbed oxygen and gas molecules successfully diffused on platinum loaded CuO surface, the doping with platinum provides numerous active sites that adsorb hydrogen sulfide gas and oxygen molecules. Therefore, it may be stated that acellent gas sensing performance of platinum -loaded CuO are primarily due to the platinum ability to accelerated electron mobility between the sensor and target gas without directly participation in the reaction. In contrast, when compared to CuO nanoflowers with 1.25 doping concentration exhibit an expanded surface area, where creating more active sites of gas adsorption. However, increasing the concentration of doping at 150wt% results in energy adsorption disruption and increased surface density, leading to fermi level changes and reduced sensor response.

S. A. Jafar, et al [18]. The vapor sensing system absorbed or desorbed surface oxygen from thin films of pure zinc oxide (ZnO) doped with zirconium (Zr), and exchanges charges between layer of the thin film and the adsorbed gas molecules. This mechanism alters the depletion regoin, as well as the surface propertis or grain boundaries. Thus, we conclude from the experiment, that the variation in electrical properties of the vapor sensor is due to the contribution oxygen. In the ZnO layer doped with Zr (3% by weight), the response to ammonia vapor is greater due to the lower contact resistance. Therefore, more electrons are released during the reaction between ammonia and oxygen species. Consequently, the resistivity decreases further compared to a pure ZnO thin film. Thus, Zr -loaded ZnO film is more sensitive to ammonia vapor than undoped ZnO film.

N. H. Al-Hardan, et al [19]. Study effect of Al loaded ZnO film for enhancing H_2 gas sensing synthesis via thermal oxidation. It is clear that the ZnO:Al thin film operates at a much lower temperature and exhibits higher response compared to undoped ZnO thin films. We believe that the improved gas

response at lower working temperature due to the incorporation of aluminum. As a result, surface activity increases aluminum has a lower ionization energy than zinc. Furthermore, modifying the surface properties may take into account another factor that could enhance sensing performance of the ZnO thin film. An increase in surface roughness will contribute to increasing the surface area -to-volume ratio, which will allow the gas penetrate further through the sensitive region in the oxide. In contrast, the surface of undoped zinc oxide is often dense, and the sensing reaction are limited to the surface, when the gas sensor is subjected to a reducing gas like H_2, a reaction occurs between the adsorbed oxygen ions on the sensor surface and H_2 gas. As the percentage of aluminum doping increases, charge carriers' concentration increases, resulting in a high output current compared to an undoped ZnO sensor.

A. Shimizu, et al [20]. In this study, silver atoms on the sensor surface enhance oxygen adsorbed, thus increasing the chemically adsorbed species such as O_2^-, therefore Ag doping of the WO_3 layer successfully improves NO sensitivity. Figure 5 illustrates the prosed model for sensing NO gas. Nitrogen oxide gas reacts with oxygen chemically adsorbed by Ag atoms in the WO_3 layer, accepting electrons from the layer. Ag atoms that appear on the surface are active, which promotes the chemical adsorption of oxygen atoms.

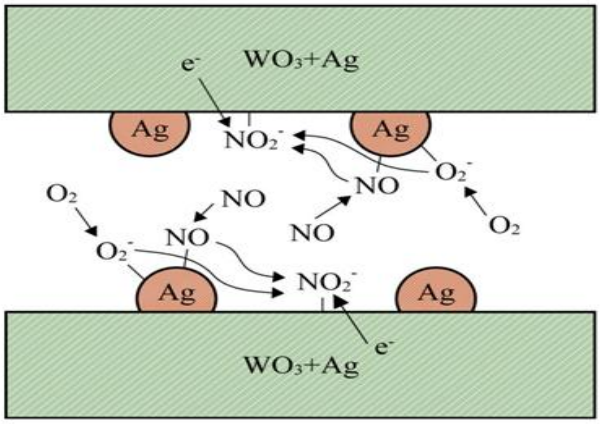

Figure 5. Prosed mechanism of NO gas sensing [20].

G. Korotcenkov et al [21]. Reported the doping effect on the sensitivity of SnO_2 thin film synthesis via spray pyrolysis. Regarding the improvement of sensor response properties of SnO_2 and SnO_2: Co thin films, we observed that the sensitivity increased at that concentration of C_{CO} ~ 2-4%. As a consequence of the substitution of tin for cobalt within the SnO_2 crystal lattice, with no the associated defects formed with the presence of cobalt between its atom, and with no observation the formation of the second cobalt oxide phase within the SnO_2 structure, which indicates that the process of doping does not cause a significant structural disturbance in the metal oxide, in contrast, it indicates that its concentration within the SnO_2 lattice is sufficient to form adequate quantities of catalytically active sites, which effectively act as O_3 decomposition centers and reducing gases influence the oxidation process and contribute to transfer of electron between the conduction band and adsorbed species in SnO_2. We hypothesize that oxygen vacancies bound Co_{sn} could be one of these centers. The concentration C_{co} ~ 2-4%, is considered consistent with the minimum values for the SnO_2: Co lattice cell size, this repersents the minimum spacing between atoms in the SnO_2 lattice, which may improve adsorption/desorption processes, this occurs on the surface of SnO_2 and controls the gas sensing effect.

Thickness

I. Kim, et al [22]. Shows a significant difference in the signal recovery rate to return to the initial level after gas detection. The adsorption reaction time between the toxic gas and the ionized oxygen is similar for both thin and thick films, ranging between 5 and 7 seconds, but there is a significant difference in the desorption reaction. The recovery time of thick film sensor is approximately 160s in this example, and the response curve gradually returns to initial signal level, while the thin film sensor exhibits rapid recovery within a short period of approximately 10s, as shown in figure 6. This difference in recovery

rate, due to thickness of the sensing layer. a thicker layer contains more pores and clusters than a thinner layer. In this case, even reactant gas is depleted oxygen and fresh oxygen are introduced, the length of the delay time required for the oxygen to penetrate the thick layer results in slow reabsorption of oxygen ions.

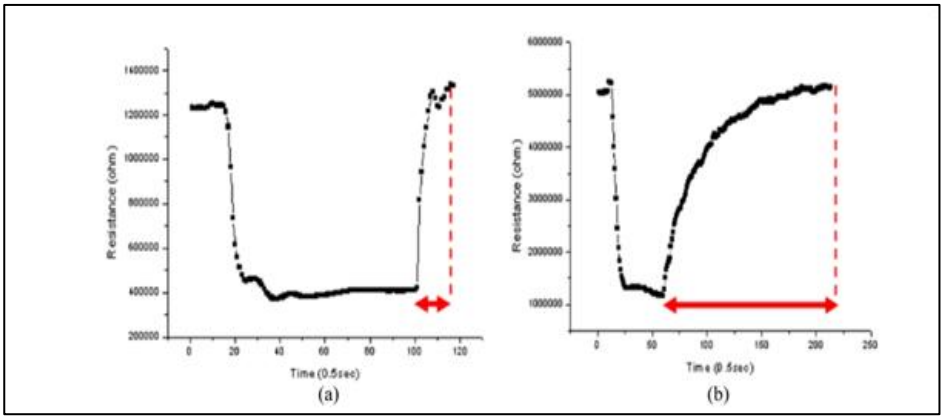

Figure 6. Recovery characteristics for (a) thin film sensor and (b) thick film sensors [22].

P. Patial, et al [23]. Study influence of thickness variation on gas sensing for ZnO thin film. The large surface area of ZnO thin films contributes to high atoms density, which can lead a to week atomic bonding and an excessively high surface energy. Furthermore, the surface morphology influences the distribution and availability of reaction sites, as well as thin films sensitivity to LPG molecules, thus improving gas detection efficiency. In addition, surface roughness contributes to an increased surface area, allowing for greater interaction of a high number of gas molecules with the film surface. 155nm thick ZnO sensor exhibits superior sensing performance due to its increased surface area and higher roughness of the sample. This enhanced gas absorption also leads increased sensitivity of film to LPG. Therefore, the surface became highly active, enhancing the absorption of more oxygen from the surrounding environment, where ZnO sensor at thickness of 155nm demonstrating a highest sensitivity of 225%.

The porosity of thin film has an effect on the adsorption and desorption processes of LPG on ZnO sensing layer. The results also showed increasing the film thickness (i.e increasing porosity) of the ZnO sensing layer in turn enhaces both the adsorption and desorption processes of LPG. Porosity, and with-it particle size, increases with increasing surface area to volume ratio up to certain limit, then the film porosity begins to decrease, which leads to decrease in the number of oxygen vacancies sites above the sensing layer. Consequently, sensing responses may degradation of composition with thickness greater than 155nm.

J. F. Chang, et al. [24]. Researcher indicated that the gas sensitivity increased with decreasing thin film thickness under 400℃. it is well established that the sensing capability of metal oxide – based semiconductor sensor depends primarily on the nature of the interaction between the target gas and the sensor surface. Accordingly, the larger the surface area of the material, stronger the interaction between the sensing layer and the adsorbed gases. Resulting in enhanced sensitivity of gas sensor. That is, grain sizes and the total surface area are at their maximum values at 65 nm film thickness. This leads to greater number of available adsorption and desorption sites. Sensitivity can be improved significantly changing surface area. Additionally, sensitivity increases as the film thickness decreases, this may also be attributed to the depletion region approaching that of film thickness.

S. Souissi, et al [25]. The sensor synthesis with different thickness in the range from 0.8 to 6.1µm, were tested 4000ppm of methanol, acetone and ethanol at an operating temperature 350℃. It was further noted that the response curve is affected by the variation in thickness. This may be to the difference in specific surface areas of the samples. In smooth films exhibiting low surface roughness (d= 0.8 µm, d=2.3 µm, d=3.2 µm with root mean roughness141nm, 207nm and 223nm respectively), the gas reaction occurs only on the surface. For high roughness and granular layer (d=4,8 µm, Rq=501nm) gas interactions can occur on the surface of at grain boundaries and individual grains. Therefore, this type of sensor is characterized by higher specific surface area, providing an abundance

of active sites for adsorption that enhance the sensor response. for the sample (d=6.1 µm, Rq=1150nm), increasing the number of cracks raises the potential barrier, weakens the sensing response and reduces the current. Increasing the number of cracks in semiconductors thin films leads to an increase resistance, which is influenced by the applied deformation and film thickness, although the cracks may act as gas trapping pathways, they are also very likely to cause an electrical breakdown that in this area. We believe that active surface that describes significantly with these cracks impede the electrical conductinity of certain parts for the material and thus affecting the gas sensor performance. We observe that the gas sensor exhibits the highest response at thickness of d=4.8 µm. Furthermore, the fastest response time is recorded for ethanol gas for all samples (T_{res} (ethanol=33s), and also the shortest recovery time (T_{rec} (ethanol=138s).

Annealing temperature

G. E. Patial, et al [26]. One of the important factors that play a fundamental role in gas sensing is the annealing temperature. Sensor materials must be thermally treated at multiple temperatures to promote crystallization and structural development. To achieve the requird electronic properties, it is necessry to reach Sufficient degree of crystallinity for gas sensor application the sensitivity was found to be at is highest wen the annealing temperature is 950℃. Annealing in air leads to increased oxygen vacancies generation which enhances gas sensitivity. The high degree of crystallization in thin films resulting from the annealing temperature effect, is also likely responsible for the improved sensing properties of these films compared to those annealed at 550℃, and 750℃. the highest sensitivities were shown at 23.4, 39, and 96 at a concentration of 80ppm H_2S at annealing temperature of 550℃, 750℃ and 95℃ respectively.

S. Sachdeva, et al [27]. The highest resistivity was found when the tungsten oxide layer is annealed at 500℃ towards acetone gas at a concentration of 20ppm. The optimal annealing temperature was calculated to be 500℃. The semiconductor films operate at a specific temperature, meaning that surface interaction between the target gas and thin films to be sensed occur at an ideal temperature.

Y. Yang, et al. [28]. The n-type SnO_2 gas sensor is strongly affected by grain size. As the grain size increases the number of energy barriers through which electrons flow across the grain boundaries decreases. Accordingly, the surface of the dense film transforms into a more porous structure, leading to increased interaction area with H_2 gas. Consequently, the sensitivity of the tin oxide film increases. After annealing process, an increase the grain size was observed, accompanied by a decrease in grain boundary defects and energy barriers. The sensor response is directly related to the gas adsorption area and the surface area; therefore, an increase in particle size leads to an increase surface area. Accordingly, the sensitivity increased with increasing annealing time reaching its maximum at 3h. The response time followed the same trend, attaining its highest value at 3h. Therefore, the SnO_2 film that has been annealed for 3h has a larger grain size and larger surface area then unannealed SnO_2 film for 1h. Figure 7 illustrates the charge transport efficiency improves with increasing particle size, leading to enhanced conductivity of the gas sensor as result of the annealing process. Additionally, grain size is considered one of the key factors affecting resistance.

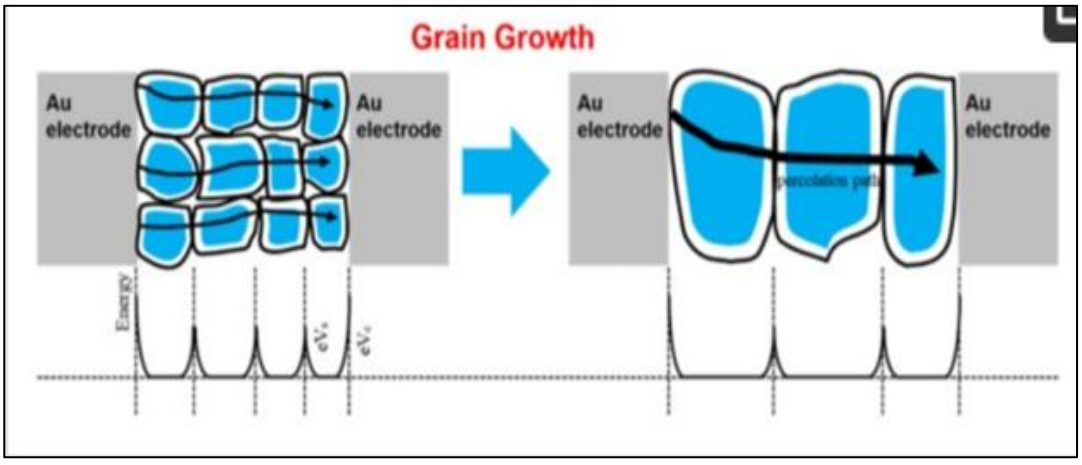

Figure 7. Schematic diagram of the boundaries of SnO_2 grains before and after annealing [28].

Grain size

G. Korotcenkov and B. Cho [29]. The result showed that heat treatment at 1000℃ leads to a significant increase in particle size within the tin oxide ceramic, increasing by more than twenty times, moving from about 12-15nm to 200-300 nm. These changes are expected the gas sensor efficiency made from these materials.

The following factors can be mentioned as potentially altering the operating properties of gas sensor:

i) modification the geometric dimensions of the particle network in the gas sensor matrix such as pores size, specific surface area and contacts area, this process are an inevitable consequence of grain growth; it occurs as a result grain coalescence. The transfer of mass from smaller grains to larger grains can stimulate expansion of the crystal contact areas and neck formation between grains illustrated in the figure (8).

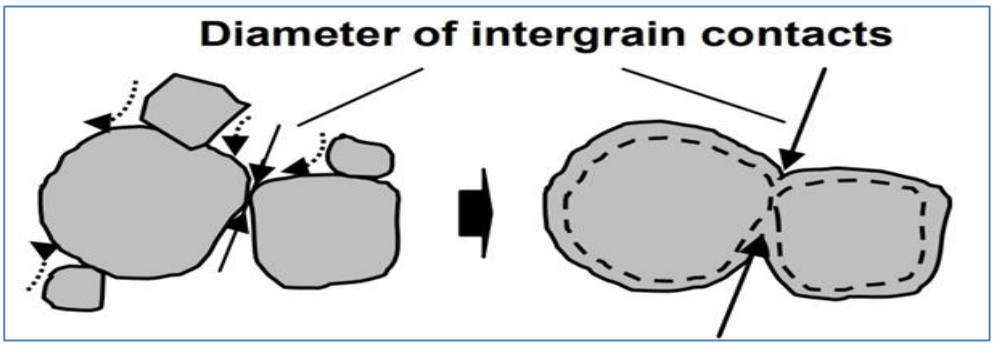

Figure 8. Diagram illustrating the evolution of the contact point geometry between grain within the gas sensing matrix during the annealing process [29].

ii) the properties of general electrophysical for the metal oxide may changes, and these changes are likely related to grain growth may involve changes to the crystal structure of the material, point defects concentration and the band gap.

iii) the catalytic and electronic properties variation of the crystal surface.

R. Savu, et al [30]. Study of the effect grain size on the gas sensor and electrical response of SnO_2. The atmosphere has a significant impact on the particle size and its grain boundary, which determines the behavior of the electrical devices is significantly affected by ambient conditions. Samples prepared using different methods showed that its electrical resistance changes considerably depending on the surrounding atmosphere, as an operating temperature as low as 150℃. The good response of the gas sensor can be attributed to larger grain size, high porosity and low initial resistance. The optimum working temperature was 200℃ at which the sensitivity improved and the response time decreased; this is attributed to an increased rate of adsorption / desorption. The recorded impedance spectra as a function of gas medium and temperature, reveal two distinct time constants associated with the grains and their boundaries. This behavior arises from surface chemical reaction and those occurring at the grain boundary in the presence of oxidizing agents in the surrounding medium. Nitrogen contributes to the removal of oxygen adsorbed on the grain surface, thereby reducing the sample's electrical resistance. Conversely oxidizing agents reduce the concentration of charge carriers located within the surface layer and across the grain boundaries, while reducing agents, by removing oxygen, increasing the concentration of charge carries.

M. Gillet et al [31]. Our results show that the response of tungsten oxide (WO_3) thin films to ozone is closely related to grain size, as the sensitivity increases approximately five-fold in films with an average grain size of 60 nm compared to those with a grain size of up to 100nm. Ozone is likely to decompose on the sensitive WO_3 surface into $O_3 \rightarrow O_2 + O \rightarrow 3O^-$ (adsorbed). Free electrons disappear when a single molecule of ozone is adsorbed onto the surface of tungsten oxide (WO_3); therefore, the electrical conductivity becomes highly sensitive as a result of the interaction between the sensing surface and ozone. It is evident that fine grained thin films, which possess high surface area-to-volume ratio, achieve increased sensitivity response. Grain size appears to be crucial factor in

determining the sensitivity of undoped WO_3 thin -film materials used as chemical sensors.

Results

Previous studies have shown that oxygen vacancies play a fundamental role in gas sensing as they act as active sites for oxygen adsorption. We observed from the studies that the content of oxygen vacancies depends on the annealing temperature in WO3 was 20.1%, 16.8% and 14.8% at annealing temperature of 400℃, 600℃ and 800℃ for 3h respectively. This can be attributed to the fact that annealing at low temperature led to week oxidation. Therefore, annealing at 400℃ increased the concentration of the high oxygen vacancies in WO3, which in turn enhance the response of the gas sensor. The researches demonstrated that the increased in the CH3COCH3 detection sensitivity of the Ag-doped TiO2 sensor (45s) was result of the catalysis performance of the Ag. In fact, silver loaded enhanced the number of available surface sites for adsorption on the TiO2 an increased the rate of electron transfer between CH3COCH3 molecules and surface of the titanium dioxide. Based on the research results, the amount of adsorption was related to the number of oxygen vacancies that are unoccupied were formed due to the difference in charge between the Ag and Zn ions, indicating the creation of more active sites for adsorption, leading to an enhanced sensor response. Study the effect carbon-doping on sensor performance of molybdenum oxide, we are observed that the electrical resistance of sensor reduces by an order of magnitude upon the addition of carbon, it is clear that adding carbon to reaction deposited molybdenum oxide films causes considerable improvement in the sensing toward ethanol.

Platinum doping of CuO provides numerous active sites that adsorb hydrogen sulfide gas and oxygen molecules. Therefore, it may be stated that excellent gas sensing performance of platinum -loaded CuO are primarily due to the platinum ability to accelerated electron mobility between the sensor and target gas without directly participation in the reaction. We also observed from the results that the silver atoms on the sensor surface enhance oxygen adsorbed, thus increasing the chemically adsorbed species such as O_2^-, therefore, Ag doping of the WO3 layer successfully improves NO sensitivity. Study influence of thickness variation on gas sensing for ZnO thin film. 155nm thick ZnO sensor exhibits superior sensing performance due to its increased surface area and higher roughness of the sample. where ZnO sensor at thickness of 155nm demonstrating a highest sensitivity of 225% toward LPG gas. This may be attributed to porosity of thin film has an effect on the adsorption and desorption processes of LPG on ZnO sensing layer.

The sensor synthesis with different thickness in the range from 0.8 to 6.1µm, were tested 4000ppm of methanol, acetone and ethanol at an operating temperature 350℃.. In smooth films exhibiting low surface roughness (d= 0.8 µm, d=2.3 µm, d=3.2 µm with root mean roughness141nm, 207nm and 223nm respectively), the gas reaction occurs only on the surface. For high roughness and granular layer (d=4,8 µm, Rq=501nm) gas interactions can occur on the surface of at grain boundaries and individual grains. Therefore, this type of sensor is characterized by higher specific surface area, providing an abundance of active sites for adsorption that enhance the sensor response.

Discussions

The presence of vacancies oxygen in the gas sensor is considered centers for the accumulation of charge carriers, which reducing their losses resulting from recombination and contributes the increasing the life time of photogenerated charge. Surface depletion layer is formed due to the trapping of electrons from conduction band by oxygen vacant sites, which in turn increases the density of chemically adsorbed oxygen species. Increasing the proportion of oxygen vacant in thin layer of metal oxide reduces the energy gap. The concentration of these vacancies varies depending on the film microstructure and growth duration. Therefore, the vacancy concentration has a substantial effect on the sensor response properties. These lattice vacant will behaves like sites that are active for the chemisorption of oxygen present in the air during the gas sensor exposure to it. The greater the number of this lattice vacant chemisorption of oxygen, the result is the reaction of many reducing gas molecules

(such as CO), which in turn leads to an improvement in the sensor response the sensing mechanism based on the magnitude of change in the electrical resistance of metal oxide. Upon exposure of metal oxide nanoparticles to the surrounding air, adsorption and desorption processes of gas molecules occur on the material surface of sensor. The oxygen molecules adsorbed on the surface of the gas sensor trap electrons from the conduction band of metal oxide. Various of oxygen ions are also formed including O_2^-,O^-,O^(2-) depending on operating temperature. Upon exposure of the sample to target gas such as acetone gas (CH3COCH3), many numbers of electrons are released as a result of the interaction between gas molecules with the adsorbed oxygen ions (O^(2-))on the sensor surface, returning to the conduction band of metal oxide. Subsequently, decrease in the depletion layer thickness lead to reduction in resistance. Oxygen vacancies act as oxygen ion acceptors in the air at high temperature. we assume the presence of oxygen vacancies in n-type metal oxide semiconductor; the oxygen vacancies are often located "deep" in band gab. Therefore, these electrons resulting from the formation oxygen vacancies do not ionize into free electrons, but remain captured at the vacancies. Due to the relatively large number of holes (main charge carriers) in p-type material, it is expected that it will be thermodynamically preferable of electrons captured in oxygen vacancies (inside the band gap) for recombination with valance band holes.

Silver loaded leads to an increase in the number of available surface sites for adsorption on the surface of TiO2, this leads to an increase in the electron exchange rate between gas molecules and sensor surface. In a CH3COCH3 atmosphere, the bonds between CH3COCH3 molecules are readily broken by Ag, promoting the activity of these molecules to react rapidly with chemisorptively adsorbed oxygen species. Furthermore, the deposition of Ag nanoparticles onto TiO2 nanorods stabilizes the fermi level of TiO2 because of electron movement from TiO2 to Ag, thus improving the sensor response to CH3COCH3.

Platinum doping with copper oxide provides numerous active sites that adsorb hydrogen sulfide gas and oxygen molecules. Therefore, it may be stated that excellent gas sensing performance of platinum -loaded CuO are primarily due to the platinum ability to accelerated electron mobility between the sensor and target gas.

The adsorption reaction time between the toxic gas and the ionized oxygen is similar for both thin and thick films, ranging between 5 and 7 seconds, but there is a significant difference in the desorption reaction. The recovery time of thick film sensor is approximately 160s in this example and the response curve gradually returns to initial signal level, while the thin film sensor exhibits rapid recovery within a short period of approximately 10s. This difference in recovery rate, due to thickness of the sensing layer. a thicker layer contains more pores and clusters than a thinner layer.

The surface morphology influences the distribution and availability of reaction sites, as well as thin films sensitivity to LPG molecules, thus improving gas detection efficiency. In addition. An increase in surface roughness will contribute to increasing the surface area -to- volume ratio, which will allow the gas penetrate further through the sensitive region in the oxide, when the gas sensor is subjected to a reducing gas like H2, a reaction occurs between the adsorbed oxygen ions on the sensor surface and H2 gas., allowing for greater interaction of a high number of gas molecules with the film surface. Accordingly, the larger the surface area of the material, stronger the interaction between the sensing layer and the adsorbed gases. Resulting in enhanced sensitivity of gas sensor. That is, grain sizes and the total surface area are at their maximum values at 65 nm film thickness. This leads to greater number of available adsorption and desorption sites. Sensitivity can be improved significantly changing surface area. Additionally, sensitivity increases as the film thickness decreases, this may also be attributed to the depletion region approaching that of film thickness.

Conclusion

1. The improved performance is resulting from the synergy effect of oxygen vacancies that enhance adsorption onto the surface and narrowing of the band gap enhance the separation of photogenerated charges.
2. The controlled preparation of WO3 films featuring a porous morphology and increased surface

oxygen vacancies has greatly enhanced the gas sensing response of the sensors.
3. The effect of doping proved to be more important than thickness of the thin film.
4. The annealing at above 300℃ in air improved crystallinity and formed high porosity have given excellent sensitivity.
5. The doping of Zr increases the number of electrons in the ZnO films, thus helping to enhanced the amount of oxygen absorption leads to increased sensitivity efficiency of the ammonia vapor sensor.

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