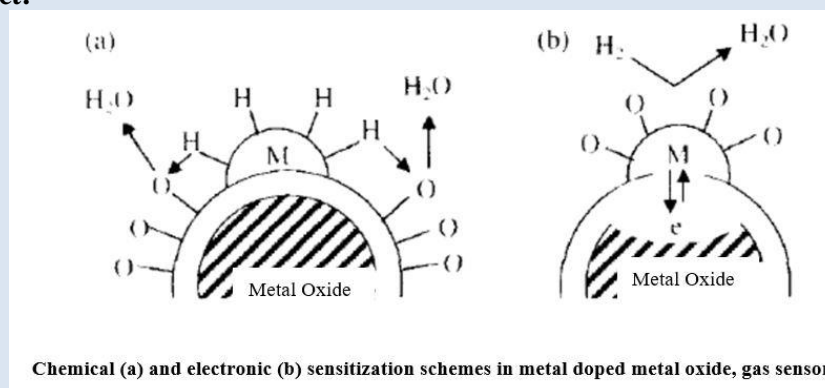## Short Review Article

Review on: TiO₂ Thin Film as a Metal Oxide Gas Sensor

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Abstract:

Titanium dioxide is an important metal oxide semiconductor (MOSs) used in many electronic applications, the most famous of which are gas sensor applications. This review discusses the techniques used for preparing the TiO₂ thin films and the effect of the crystalline phases in which this compound forms, on the gas sensing properties. There are three phases to crystallize titanium dioxides, brookite, anatase, and rutile phase. Amongst these varied phases of crystal, the greatest steady main phase is rutile. The phase of anatase and brookite are usually more stable than the rutile phase as the surface energy of them is less than that of the rutile. Therefore, the applications of sensing by anatase TiO₂ and rutile TiO₂ were fully studied. TiO₂ characterizations were established on surface reactions using oxidizing or reducing gases, which; therefore, influences the conductivity of the film. Titanium dioxide gas sensors have healthier steadiness and sensitivity at high temperature compared with that of the other metal oxides. Surveys on titanium dioxide thin film applied in gas sensor devices used in a varied range of applications such as sensor devices, dye-sensitized solar cells, and catalysis. The gas sensor is a function of the crystal structure, particle size, morphology, and the method of synthesis. In this work, characteristic of the titanium dioxide films investigated using various techniques, as reported by many researchers. The aim of this study was to review previous studies through which the best properties can obtained to manufacture TiO₂ gas sensor thin films with high sensitivity.

Graphical Abstract:

Chemical (a) and electronic (b) sensitization schemes in metal doped metal oxide, gas sensor

Biography:

Jamal Malallah Rzaij was born in Iraq, in 1972. He completed her BSc degree from University of Anbar in physics. He received his Master's in solid-state physics at the same university and PhD in solid-state physics/Nanostructures at the Tikrit university. He has published more than 15 papers. He is working lecturer as an Assistant Professor at University of Anbar, Iraq. His area of research interest is, Nanostructures, thin films and gas sensors.

Amina Mohsen Abass was born in Iraq (Baghdad), in 1978.She completed her BSc degree from University of Baghdad in Chemistry .She is at the end of her Master's Degree from University of Baghdad in Analytical Chemistry. She has published more than 18 papers .She is working lecturer as an Assistant Professor in Al-Nahrain University, College of Science, Baghdad. Here area of research interest is, Ion selective electrode, sensors and electrochemistry.

1. Introduction

It is very important to study the physical and chemical properties of the compounds involved in the formation of gas sensors to reach the best results in detecting multiple types of gases [1-4]. These sensors usually designed in the form of an electronic or electrical device that senses a sign and converts it to the alternative system [5-11]. Chemical gas sensors classify the gases by the measuring the breakdown voltage, (the electric field at which the gas is ionized), which is definite gases [12-15]. The device gives a specific amount of current that can determine the gas concentration. These types of gas sensors are necessary with attention to the users that it is working below atmospheric conditions, ease of their use, flexibility connected to their production, and low cost [16-20]. The types of gas sensors that are widely used can be classified into; metal oxide gas sensors, acoustic wave gas sensors, capacitance gas sensors, optical gas sensors, and calorimetric gas sensors. Under the weather conditions and the widespread use of machines that emit the harmful gases in addition to gases emitted by factories and vehicle exhausts, the detection of these gases became necessary. Researchers were have paid attention to sensors that are flexible in production, low cost, simplicity of using, and a good detectable for many types of gases and their concentrations [21-23]. The present study was focused on metal oxide gas sensors (chemiresistors) such as CuO, NiO, ZnO, and TiO_2. Metal oxides were well-known as the probable sensitive resources [24, 25]. They were come to be to the marketplace by Taguchi [26] who originated the grates company of SMOXs sensors. The attainments of these devices are presented in Table 1.

Table 1. Characterization techniques for nanoparticle properties.

Entry	Techniques	Properties	Ref.
1	Fee and implementation	Better fee– implementation ratio they are cheap(the range of value is a little euros for sensor)	[26]
2	Accessibility	Accessible (a direct connection through the resistance of sensor and the concentration of the aim gas)	[26]
3	Sensitivity	Exact sensitive (in general being capable to determine downward to a little percent ppb, or also a little ppm).	[26]
4	Stability	More stability (by way of described lifetime encompassing into decades).	[26]
5	Combination	Ease to combine in groups for extra aspiring analytical responsibilities.	[26]
6	Operating temperature	Sensibly a little power depletion when deposited in micro-machined thin films by using a varied temperature type (recognized by optimizing the better working).	[26]

There are two kinds of metal oxide including, transition -metal oxides (Fe_2O_3, NiO, and Cr_2O_3), and non-transition metal oxides, which contain metal oxides as pre-transition (Al_2O_3), and metal oxides as post-transition (ZnO, SnO_2). Metal oxides as pre-transition (MgO) are probable to be extremely inactive, for the reason that they have a great energy band gap, also, from the difficult to form the electrons and holes [24].

They are rarely nominated as gas sensor substances due to their complications in measurements of electrical conductivity. Transition metal oxides have different behavior due to the small difference in the energy between a cation (d^n) configuration and the configuration of d^{n-1} or d^{n+1}. They can variation formulae in some unlike types of oxides. Therefore, they are extra sensitive than metal oxides as pre-
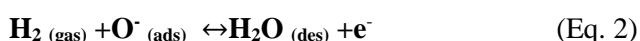
transition to environment. On the other hand, instability of structure and non-optimality of extra factors imperative for limit of conductometric gas sensors and application. Just transition-metal oxides with d^{10} and d^0 electronic arrangements discover their actual gas sensor application. The d^0 arrangement is institute in dual transition-metal oxides [27].

2. Gas detection

The gas detection of SMOXs gas sensors based on the principle at 150 °C - 400 °C, is adsorbed the oxygen on the surface of the metal oxides by trapping electrons which are the greater number of charge carriers, then the sensor's resistance will be increase (for n-type materials), or else reducing it (for p-type materials) [24]. The change in the sensor resistance is usually caused by the interaction between gas in the atmosphere and oxygen on the semiconductor surface, therefore the resistance changing will appear as a signal (sensor signs) [28]. The magnitude of this signal correlates on the gas concentration. Therefore, to obtain a highly sensitive sensor, two characteristics must be studied: the chemical reaction between the gas and the surface of the material and the transfer of this reaction to equivalent changes in the electric resistance of the sensor [29]. The mechanism of sensing for metal oxide is fabricated on the surface reaction, by the gas, through variations its conductivity and atmosphere.

On the surface of the positive semiconductor of type (p-type) when exposed to oxidizing gas, Oxygen will be adsorbed by the following equations [24].

$$O_{2(gas)} + 2e^- \leftrightarrow 2O_{(ads)} \qquad \text{(Eq.1)}$$

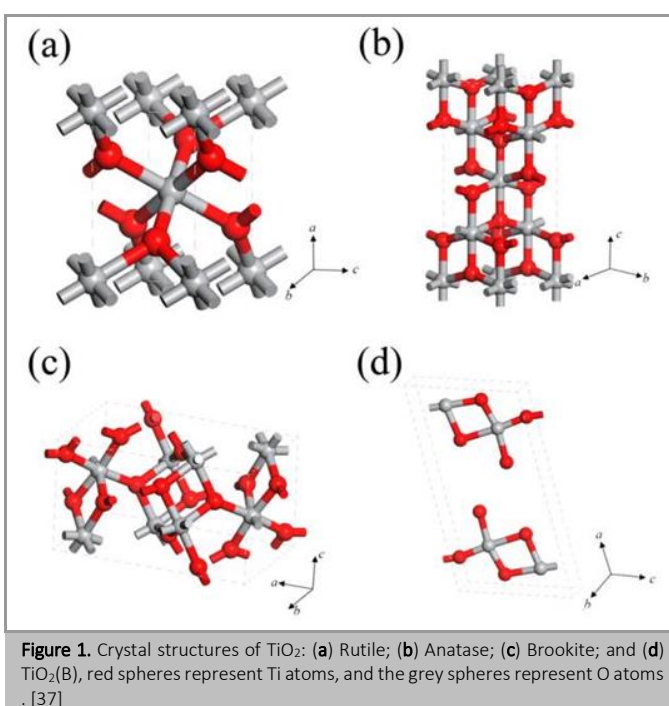$$H_{2\,(gas)} + O^-_{\,(ads)} \leftrightarrow H_2O_{\,(des)} + e^- \qquad \text{(Eq. 2)}$$

The electrons are injected back to the conductive band, partly or totally. Thus, the semiconductor resistance may decrease, results in enhancing the electrical conductivity. A reverse process will occur when exposed to a reducing gas leading to an increase in its electrical resistance. If the semiconductor is of a negative type (n- type), the results will be exactly the opposite [30-33]. The researchers were demonstrated that the properties of the gas sensor depend on the surface morphology and the dopant concentrations added to TiO_2 films.

B. Comert [34] pointed out that the sensors fabricated from titanium dioxide thin film at high temperatures possess low sensitivity. This was due to the fact that, the grain size was not small enough to increase the surface area of the film's exposure to methane gas Joy Tan *et al*. [35] 100 nm of un-doped TiO_2 and doped with Au thin film were prepared, they were discovered that adding gold to titanium films led to a significantly increased sensitivity to carbon monoxide gas. The reason was that the added gold atoms played the

catalyst role for the surfaces of the prepared films. Figure 1 shows the structure of TiO_2.

3. TiO_2 structure

TiO_2 primarily existents in three forms including, the brookite phase (orthorhombic), anatase phase (tetragonal), and rutile phase (tetragonal), as shown in Figure 1a-c, with energy gap equal to 2.96, 3.2, and 3.02 eV, respectively. In addition, the over declared three phases of crystal, there be a present added phase, TiO_2 (B) (monoclinic). Figure 1d illustrates the TiO_2 (B) layer configuration. Therefore, the exact capability is greater and the density is lower compared with that of the former phases. Among these varied phases of crystal, the greatest steady main phase is rutile, while for nanomaterials [36].

Figure 1. Crystal structures of TiO_2: (**a**) Rutile; (**b**) Anatase; (**c**) Brookite; and (**d**) TiO_2(B), red spheres represent Ti atoms, and the grey spheres represent O atoms . [37]

The phase of anatase and brookite are usually more stable than the rutile phase because the surface energy of them is less than that of the rutile. For practical applications, TiO_2 preparations films are prepared such as the annealing time, are usually artificial by the phases of crystal, which can be obtained by controlling the factors in which these construction of the structure growth, preparation temperature, and pH of the solution. Therefore, the applications of sensing by anatase TiO_2 and rutile TiO_2 are extremely studied [38]. TiO_2 material has grown excessive import appearing in the subject of gas sensing and several scientific sets are in a short time operational on this substantial specifically on its variety nanostructures. Its characterizations are established on surface reactions using oxidizing or reducing gases, which, therefore, influences the conductivity of the film. In addition, absorption by ultraviolet photon, an electron-hole pair

that can ease oxidation as well as reduction chemistry on the surface of the material is created in the film. Redox reactions lead to hygienic the surface by the way of breaking down organic pollutants to formula primarily H_2O and CO_2 molecules. TiO_2 films, in addition, validate the capability to switch from hydrophobic to hydrophilic surfaces afterward irradiation with UV light, which, both with its properties of photocatalytic, has resulted in self-cleaning competences and validating antifogging [39]. TiO_2 was selected as a thin film for the reason that is electrically isolating with very height resistivity, however, the sub oxidized TiO_2 with an additional of titanium is an n-type semiconductor within unique characterizations, showing the fault instability and O/Ti stoichiometry take an imperative factor in the characterizations of electrical [40]. Some other properties of TiO_2 are shown in Table 2.

Table 2. Properties of titanium oxide.

Entry	Techniques	Properties	Ref.
1	Conductivity	With the performing of titanium dioxide as a semiconductor, when its temperature is increasing, fast increases of the conductivity.	[35]
2	Boiling and Melting points	The point of melting for titanium dioxide is associated with the cleanliness of the titanium dioxide. Just rutile TiO_2 has a boiling point and melting point, a melting point of 1850℃, the melting point in oxygen-rich is 1879℃.	[35]
3	Stable of Thermal	about 0.01% to 0.12%.the butter thermal stability of Titanium dioxide	[35]
4	Virtual density	In the normally was used white color, the minimum is the relative density of titanium dioxide.	[35]
5	Solubility	The solubility is relating to the solutes for titanium dioxide.	[35]
6	Permittivity	Titanium dioxide has excellent electrical characterization because it has the high dielectric constant. It is about only 48 lower permittivity for anatase titanium dioxide.	[35]

4. TiO_2 as a gas sensor

TiO_2 has a wide range of applications as gas sensors counting in a medical controller and particular environmental checking method and characteristic analysis. While specific sensors generally cannot achieve such tasks of complex, novel instruments, for instance, noses of electronic, have been fabricated, which characteristically use many sensors, wholly of which work within one of different probable signal transduction principles [41]. On the other hand, in more applications to such sensor selections are stayed not enough in their working, if associated with recognized instruments for analytical chemistry such as mass spectrometer couplings/gas chromatography (GC/MS). The major problematic results as of the detail that the specific sensors commonly indication drift, are not sensitive adequate, and notice just sure classes of molecules [20]. List of titanium metal oxides and their reply to dissimilar gaseous types and toxic vapors are presented in Table 3.

Table 3. Types of TiO_2 thin film.

TiO_2 with additives	Preparation Technique	Gas Sensing	Operating Temp.	Range of Detection Limit	Sensing Element Form	Response Time	Ref.
TiO_2	Spin coating	NH_3 gas-sensing to measure gases: H_2S NO, CH_3OH and C_2H_5OH	200°C	20-100 ppm	Nanocrystalline titanium oxide thin films	-	[42]
TiO_2	Sol-gel	MoO_3-TiO_2 to measure gases: O_2,CO,NO_2	400°C	1.1-2.9 ppm for CO,NO_2 gases	MoO_3-TiO_2 thin film	15 min	[43]
TiO_2	Sol-gel	Petroleum Gas	-	-	Nanostructured Titania	240,248 sec	[44]

Continued

TiO_2	Sol-gel spin coating	Silver-Titanium Oxide to measure CO	300°C	-	Silver Doped Titanium Oxide Thin films	-	[45]
TiO_2	Assisted by UV illumination	NO_2 sensor to measure NO_2	-	100-500 ppm	TiO_2 thin film	5 min	[46]
TiO_2	RF magnetron sputtering method	Carbon Monoxide for CO gas	230-320 °C	60-125 ppm	Nanocrystalline with a Langasite Substrate	20 sec	[37]
TiO_2	Synthesis of highly-ordered TiO_2 nanotubes for a hydrogen sensor	Anodic oxidation of a titanium foil in an aqueous solution for H_2 gas	20-150°C	20-1000 ppm	nanotubes for a hydrogen sensor	90 min	[47]
TiO_2	Flame spray synthesis (FSS)	Hydrogen sensing	700°C	-	TiO_2-Based Nanomaterials	-	[48]
TiO_2	ZnO doped TiO_2. TiO_2/ZnO layers	Gas-sensing characterizations toward acetone, ammonia, ethanol, CO, and NO_2	~ 400°C	-	TiO_2-ZnO Based Thin Film	-	[49]
TiO_2	Rf reactive sputtering from Ti:SnO$_2$ and Sn:TiO$_2$ targets	TiO2–SnO2 sensors to hydrogen	473-873 K.	100-6000 ppm	TiO_2–SnO_2 thin films	-	[50]
TiO_2	RF Sputtering	Titanium Dioxide as Methane Gas Sensors	50-200°C	-	Thin Films	-	[51]
TiO_2	Atomic Layer Deposition	Al/TiO_2/A$_{12}$O$_3$/p-Si gas sensor for CO gas	27-177°C	10-60ppm	Gas Sensor by Atomic Layer Deposition at low concentration	19-26 sec	[52]
TiO_2	Spray pyrolysis	TiO_2 films for acetone, ethanol, methane, and liquefied petroleum gas	270°C	-	Thin films	-	[53]
TiO_2	Impedance spectroscopy analysis	TiO_2 thin film	200-450°C	-	Thin film	120 sec	[54]
TiO_2	Chemical spray pyrolysis	TiO_2 thin films for hydrogen gas	550°C	-	Nanocrystalline Pt-doped TiO_2 thin films	-	[55]
TiO_2	Magnetron sputtering and subsequently annealed	TiO_2 thin films for hydrogen gas	250-450°C	300-10000 ppm	nanocrystalline TiO_2 thin films	-	[56]
TiO_2	hydrothermal treatment for the detection of organic gases	TiO_2 nanotubes for toluene	500°C	-	TiO_2 nanotubes	-	[57]

5. Conclusion

In this review, the focus was on showing the effect of crystal structure, operating temperature, and the doping with semiconductor oxides effect on the sensor properties of TiO_2 thin films. The sensors fabricated from titanium dioxide thin film at high temperatures possess low sensitivity. Some characteristics of the titanium dioxide thin films such as operation temperature, range of detection, and response time at 50 ℃ -200 ℃ were discussed. The gas sensitivity of the film is generally determined by the resistance variation of films on gas experience, or else might possibly definite as the fraction of its resistance in the air to its stable formal importance in the occurrence of gas. As there were several sensor films at different operating temperatures, thus, at relatively low temperature, the sensitivity of the substance is therefore very lower. The dominant process becomes the adsorption of O^-, when the temperature increases, formerly, increases in sensitivity for the material. Time response was found to be based on the sensor properties such as electrode geometry, crystallite size, diffusion rates, additives, and electrode position. In addition, the response time at the lower value revealed a butter sensor.

Acknowledgment

Disclosure statement

No potential conflict of interest was reported by the authors.

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