Review on: TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ and rutile TiO$_2$ were fully studied. TiO$_2$ 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 TiO$_2$ gas sensor thin films with high sensitivity.

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Keywords: TiO$_2$, Metal oxide; Semiconductor; Thin films; Gas sensor

Graphical Abstract:

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.

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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 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 grate company of SMOXs sensors. The attainments of these devices are presented in Table 1.

| 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$_2$O$_3$, NiO, and Cr$_2$O$_3$), and non-transition metal oxides, which contain metal oxides as pre-transition (Al$_2$O$_3$), 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].

$$\text{O}_2^{(\text{gas})}+2e^{-} \leftrightarrow 2\text{O}^{(\text{ads})} \quad (\text{Eq.1})$$

$$\text{H}_2^{(\text{gas})} + \text{O}^{(\text{ads})} \leftrightarrow \text{H}_2\text{O}^{(\text{des})} + e^{-} \quad (\text{Eq.2})$$

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 sensitivitiy 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 exists 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](image)

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 characterizationes 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\textsubscript{2}O and CO\textsubscript{2} molecules. TiO\textsubscript{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\textsubscript{2} was selected as a thin film for the reason that is electrically isolating with very height resistivity, however, the sub oxidized TiO\textsubscript{2} with an additional of titanium is an n-type semiconductor within unique characterizations, showing the fault instabillity and O/Ti stoichiometry take an imperative factor in the characterizations of electrical [40]. Some other properties of TiO\textsubscript{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\textsubscript{2} has a boiling point and melting point, a melting point of 1850°C, the melting point in oxygen-rich is 1879°C. | [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\textsubscript{2} as a gas sensor**

TiO\textsubscript{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\textsubscript{2} thin film.**

| TiO\textsubscript{2} with additives | Preparation Technique | Gas Sensing | Operat ing Temp. | Range of Detection Limit | Sensing Element Form | Response Time | Ref. |
|----------------------------------|-----------------------|-------------|------------------|--------------------------|---------------------|--------------|------|
| TiO\textsubscript{2}            | Spin coating          | NH\textsubscript{3} gas-sensing to measure gases: H\textsubscript{2}S NO, CH\textsubscript{3}OH and C\textsubscript{2}H\textsubscript{5}OH | 200°C | 20-100 ppm | Nanocrystalline titanium oxide thin films | - | [42] |
| TiO\textsubscript{2}            | Sol-gel               | MoO\textsubscript{3}-TiO\textsubscript{2} to measure gases: O\textsubscript{2}, CO, NO\textsubscript{2} | 400°C | 1.1-2.9 ppm for CO,NO\textsubscript{2} | MoO\textsubscript{3}-TiO\textsubscript{2} thin film | 15 min | [43] |
| TiO\textsubscript{2}            | Sol-gel               | Petroleum Gas | - | - | Nanostructured Titania | 240,248 sec | [44] |
| TiO₂                | Method/Coating                          | TiO₂ – SnO₂ sensors to hydrogen | Temperature | Response Time |
|---------------------|-----------------------------------------|---------------------------------|-------------|---------------|
| Sol-gel spin coating| Silver-Titanium Oxide to measure CO    | 300°C                           | -           | 5 min         |
| Assisted by UV illumination | NO₂ sensor to measure NO₂   | 100-500 ppm                     | TiO₂ thin film | -             |
| RF magnetron sputtering method | Carbon Monoxide for CO gas | 230-320 °C                      | 20-125 ppm  | 20 sec        |
| Synthesis of highly-ordered TiO₂ nanotubes for a hydrogen sensor | Anodic oxidation of a titanium foil in an aqueous solution for H₂ gas | 20-150°C | 20-1000 ppm | 90 min |
| Flame spray synthesis (FSS) | Hydrogen sensing | 700°C | - | TiO₂-Based Nanomaterials |
| ZnO doped TiO₂ | Titanium Dioxide as Methane Gas Sensors | 50-200°C | - | Thin Films |
| Rf reactive sputtering from Ti:SnO₂ and Sn:TiO₂ targets | TiO₂–SnO₂ sensors to hydrogen | 473-873 K. | 100-6000 ppm | - |
| RF Sputtering | Al/TiO₂/Al₂O₃/p-Si gas sensor for CO gas | 27-177°C | 10-60 ppm | Gas Sensor by Atomic Layer Deposition at low concentration |
| Spray pyrolysis | TiO₂ films for acetone, ethanol, methane, and liquefied petroleum gas | 270°C | - | Thin films |
| Impedance spectroscopy analysis | TiO₂ thin film | 200-450°C | - | Thin film |
| Chemical spray pyrolysis | TiO₂ thin films for hydrogen gas | 550°C | - | Nanocrystalline Pt-doped TiO₂ thin films |
| Magnetron sputtering and subsequently annealed hydrothermal treatment for the detection of organic gases | TiO₂ thin films for hydrogen gas | 250-450°C | 300-10000 ppm | - |
| Chemical spray pyrolysis | TiO₂ nanotubes for toluene | 500°C | - | TiO₂ nanotubes |
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 TiO₂ 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 °C -200 °C 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 O₂, 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.

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No potential conflict of interest was reported by the authors.

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