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Research Article

Study the Characteristics of TiO_2: Ag Pure and Doped Films as Gas Sensor

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Abstract

In this research, thin films of titanium dioxide were prepared and doped with certain doping percentages (2, 4, 6)% of silver. The films were prepared at a temperature of (400°C) and deposited on glass floors using thermal chemical spraying technique, after which it was annealed. At a temperature of (300Cº) for two hours, the results of the X-ray examination showed that the prepared pure and silver-dotted titanium dioxide films possess a polycrystalline structure of the Anatase type, and we note an increase in the growth of crystalline levels and their intensity with the increase in the percentage of doping. The results of the optical properties showed that the doping led to a decrease in transmittance and energy gap and an increase in absorbance, while the results of the Hall effect showed a clear increase in the concentration of carriers and a decrease in mobility values at room temperature with an increase in doping ratios. The results of gas sensitization to nitrogen dioxide showed that the sensitivity increases with increasing doping, where the best sensitivity appeared at (6%) of doping at a temperature of (200Cº).

Introduction

Semiconductor devices have evolved from millimeter-sized devices capable of electrical processing (as in transistors) to micrometer-sized devices that can process electricity and light (such as light-emitting devices), [1]. The conductors are called transparent conduction oxides and they are called for short (TCOs). (Transparent Conductive Oxides), which are composed of composite semiconductors consisting of metal combined with oxygen such as TiO_2,In_2O_3, ZnO SnO_2 [2]. These materials combine two advantages as they are characterized by their high conductivity and high optical transmittance (transparent), extending the transmittance spectrum in them Between 400-1500 (nm) [3], all of this, we see that recent research refers to the field (TCOs) because of its technological importance and versatility in solar cells and transparent transistors [4].

Titanium dioxide (TiO_2) is a semiconductor oxide that contains a wide and abundant energy gap in the earth's crust. It is the seventh most abundant element in the earth's crust. It produces about four million tons per year and half of the production is used as a pigment and a quarter of the investment in the plastic industry in travel bags and doors. The refrigerator is an industrial material for fibers and ceramics, as well as the manufacture of papers. Despite its abundance in the earth's crust, it is not found in a pure form, as it is associated with oxides or with other metals. [6,5] Titanium dioxide (TiO_2) is a photocatalytic material that was discovered by (Honda and fuijshina) and the electric polarization of titanium oxide in water was observed in 1972. In recent years, scientists have been widely interested in the use of titanium dioxide in environmental applications. [7] Titanium dioxide has three phases: rutile, Anatase, brookite and rutile, the most stable phases of titanium dioxide [8].

Silver has been a precious decorative metal since ancient times, silver is not a highly reactive metal and is insoluble in dilute acids and alkalis, but soluble in concentrated nitric acid or sulfuric acid, and does not react with oxygen or water at room temperature. Sulfur and sulfide corrode silver, and silver may lose its luster due to the formation of silver sulfide on the surface of the metal. Additionally, silver, a bleaching agent that contains the right amount of sulfur as a protein component, will quickly tarnish. It also tarnishes the small amounts of sulfides naturally present in the atmosphere, which are added to household gases (such as hydrogen sulfide). Silver black sulfide is one of the most insoluble salts in aqueous solutions, and this feature is used to separate silver ions from other positive ions [9].

Theoretical Part-:

1- Hall effect

The Hall effect is one of the most common methods for measuring the density of charge carriers directly, and it is considered a convincing way to prove the existence of gaps as charge carriers. Magnetic (Bz), and when an electric field is applied to an n-type semiconductor in the direction X and a magnetic field perpendicular to it in the direction Z, this field will deviate from its original path according to the right-hand rule due to the generation of the Lorenz force F_L, which changes the direction of the charge carriers, which leads to the accumulation of charge carriers The negative (electrons) collect them at the lower side of the semiconductor and collect the positive charge carriers (holes) at the upper side, and by their accumulation, a Hall potential difference V_H is created, accompanied by an electric field called the E_H Hall field [11.10]. Through the slope of the linear relationship between the Hall voltage and the outgoing current and through an appropriate thickness (t). The concept of the Hall coefficient R_H (Hall coefficient) appears through the following relationship [10].

$$R_H = V_H/I_H .t/B_z \quad \text{………………..1}$$

Where the sign of the Hall coefficient is negative for the n-type semiconductor and it is expressed by the following equation [10].

$$R_H = - r/nq \quad \text{………………………2}$$

Where (n) the concentration of the carriers, (q) the charge of electrons, (r) the scattering factor ($r \leq 1$)

Therefore, the concentration of charge carriers can be calculated through the following equation:

$$n= -1/R_{Hq} \text{ ……. } n>>p \text{ ………………3}$$

Hall kinetics can be found through Hall coefficient and Hall conductivity according to the following relationship [10]:

$$\mu_H=\sigma/ne = \sigma|R_H| \text{ ……………..……4}$$

Whereas:

(σ) Conductivity is measured in units-1 (Ω . cm)

(μ_H) Hall mobility, measured in units (V.s/ cm2).

2- Sensitivity:

Sensitivity is defined as the rate of change in the resistance of the thin film in the presence and absence of gas, and sensitivity is affected by several factors, including: relative humidity, temperature of the sensors, the response time of the sensitivity, the time of exposure of the films to the gas, the composition of the gas, and the thickness of the film. The sensitivity is symbolized by the symbol (S). It can be expressed by the following relationship [14,13,12].

$$S = \frac{|\Delta R|}{R_o} \text{ X } 100\% = \frac{R_{gas} - R_{air}}{R_{air}} \text{ X } 100\ \% \text{ …………..….. 5}$$

Since: (ΔR) is the change in electrical resistance. (R_{air}),the amount of resistance in dry air. (R_{gas}) resistance when entering gas.

3-Physical and Chemical Properties of NO_2 Gas:

NO_2 is a reddish-brown gas that is not combustible, but it helps to burn. It is a poisonous gas with a strong suffocating smell. The symbol (NO_x) is used to denote nitrogen oxides (NO_2, NO), which are the two gases that are referred to in air pollution because they are toxic and participate in the light reactions that occur In the air that leads to the formation of fog, and this oxide is emitted to the atmosphere through natural sources resulting from the decomposition of nitrogen-containing compounds in the soil by bacteria and lightning, or different human activities such as burning fuel in cars and power plants where large quantities are produced and in a narrow space , which leads to high concentrations, and this makes it polluting and harmful to the environment [15].

Practical Part

1- Prepare a solution of titanium dioxide (TiO_2):-

A solution of titanium dioxide with molarity (0.3 mol/l and a volume of (50 ml) of iodized water was prepared using the following relationship: [16]:

$$W_t = \frac{M*M_w*V}{1000} \qquad ....6$$

Whereas:

M = molarity (mol/l)

M_w = molecular weight (g/mol)

V = volume (ml)

W_t = weight (g)

After that, the solution is mixed using a magnetic stirrer for a period of (30-60) min to complete the dissolution process.

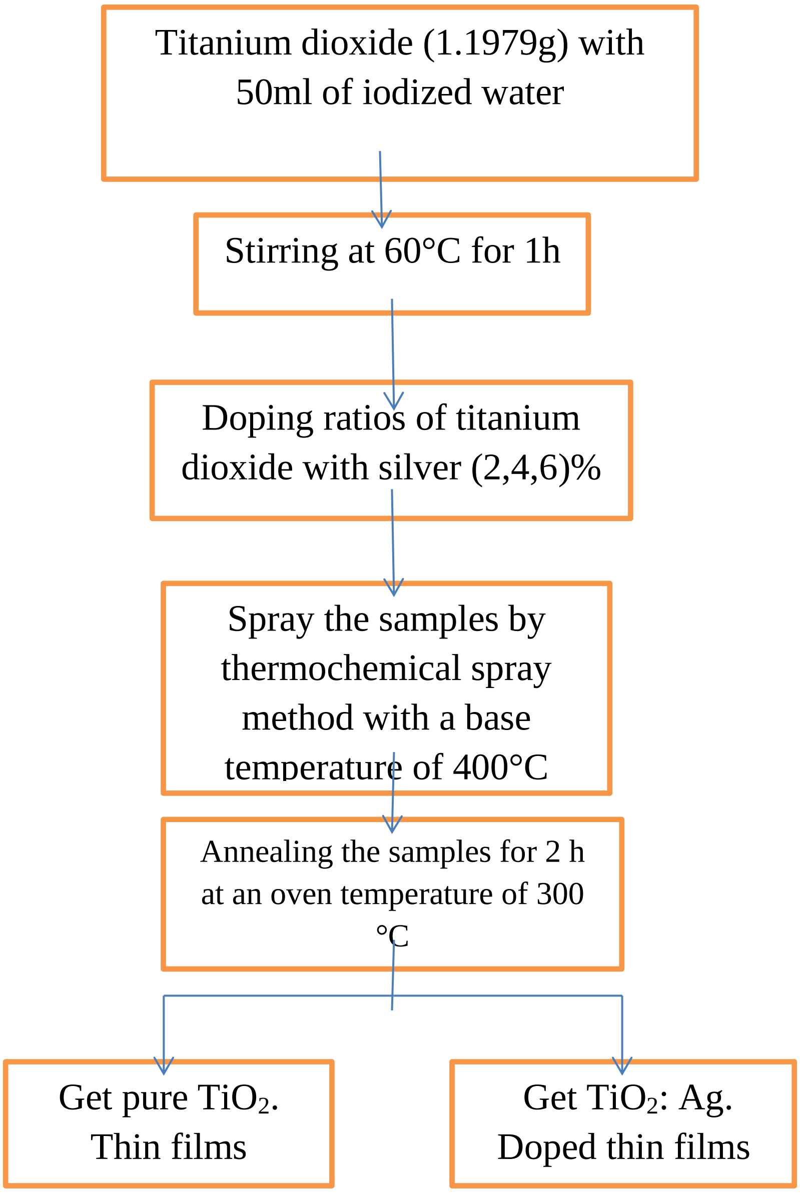
2-Preparation of a solution of titanium dioxide doped with silver ($Ag:TiO_2$):-

A silver substance with a molecular weight (169.87 g) was used and it is in the form of a white powder that quickly dissolves in (50ml) of Ionic water with a molarity of 0.3 mol/l and is added with a percentage of doping of %(2, 4, 6) of the total of the titanium dioxide mixture).

3- Thin films Preparing:

In this research, films were prepared by thermal chemical spraying method using one type of ultra-thin glass bases of Chinese origin, with a thickness of (1.2 mm) and an area of (2.5 * 2.5 mm). The spraying process is carried out at a temperature of (400) ℃ for the glass bases and then annealing the prepared films with a degree of temperature (300 ℃) for a period of two hours and then get the required films.

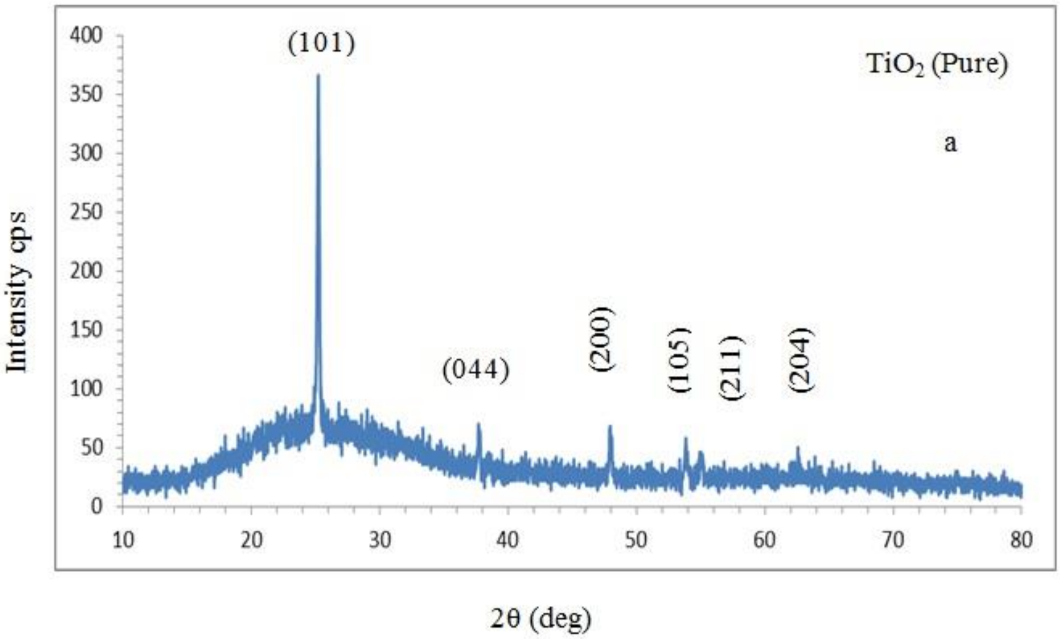
4- The diagram shows the stages of deposition of thin films prepared in the study

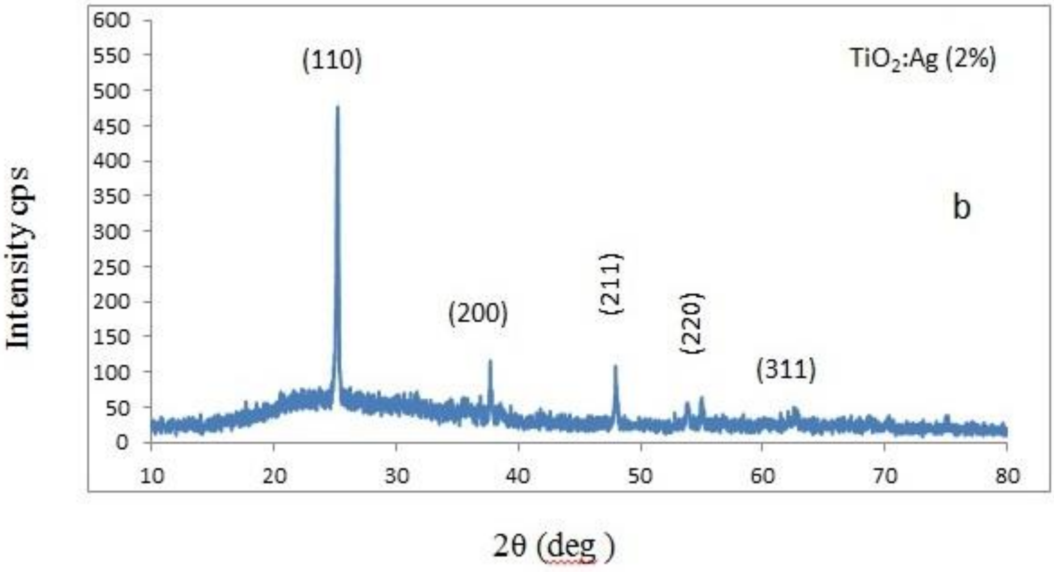


Results and Desiccation:

The results of the diagnosis by X-ray diffraction technique of the prepared (TiO_2: Ag) thin films stated pure and dotted with percentages (2, 4, 6)%. Figure (1-a) which represents the X-ray diffraction spectrum of the pure (TiO_2) film shows the presence of six clear peaks (Peaks) For the levels (101), (004), (200), (105), (211), (204) at angles 25.24°, 37.74°, 47.97°, 53.83°, 55.00°, 62.62°, respectively, where we note that the dominant phase for Anatase, it is (101) at the angle of 25.24° on the rutile and Rockite phases, which makes it the preferential directional level of crystal growth where the diffraction intensity is the highest and it was found to be of a polycrystalline structure. [18.17].

Figures (1- b-c-d) represent the X-ray diffraction spectrum of the doped thin films, where we notice an increase in the crystalline levels growth and intensity with the increase in the percentage of doping. As the doping process of titanium oxide (TiO_2) did not lead to a change in the shape of the crystal structure and the phase it formed. The film material worked as a catalyst for the growth and regularity of the alignment and construction of crystals in the same direction of crystal growth (101) and this behavior corresponds with the researchers [20.19]. As well as the appearance of the crystal plane (200) for silver (Ag), (220) for silver dioxide (Ag_2O) and we note the appearance of silver dioxide peaks (Ag_2O) because over time it is possible to grow a layer of oxide as the crust of silver cores on the surface [21].




Intensity cps
600
550
500
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350
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0
10
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30
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2θ (deg)
(110)
(200)
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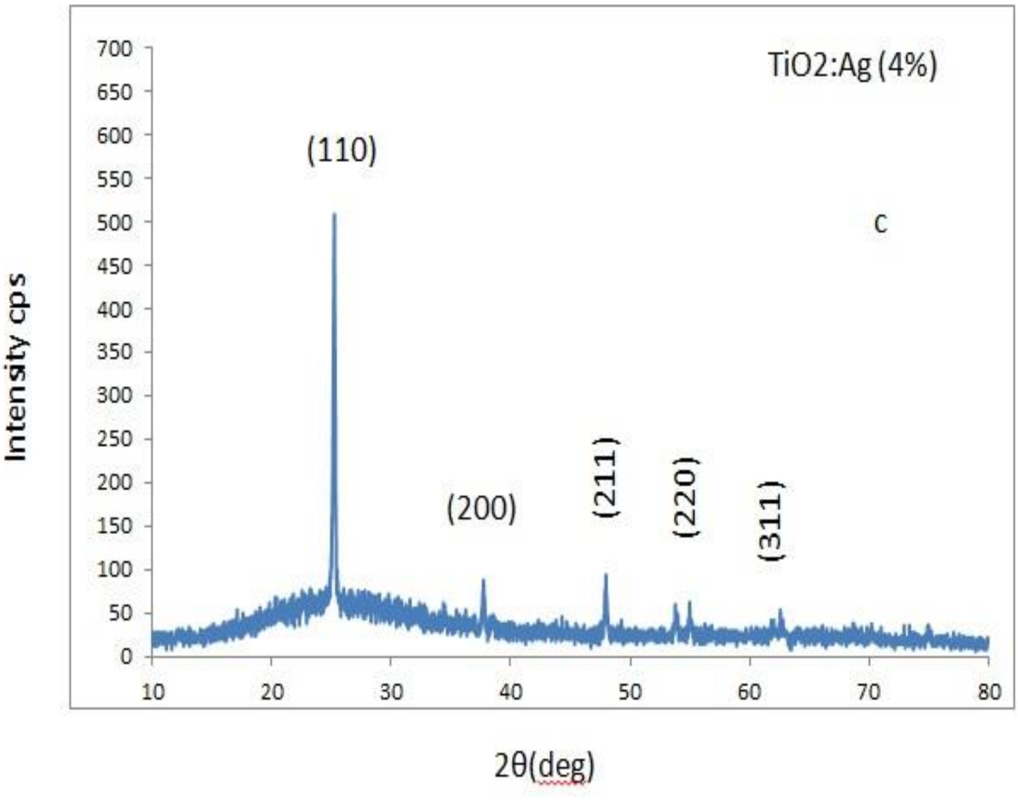
(220)
(311)
TiO₂:Ag (2%)
b


Intensity cps
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2θ(deg)
(110)
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(311)
TiO2:Ag (4%)
c

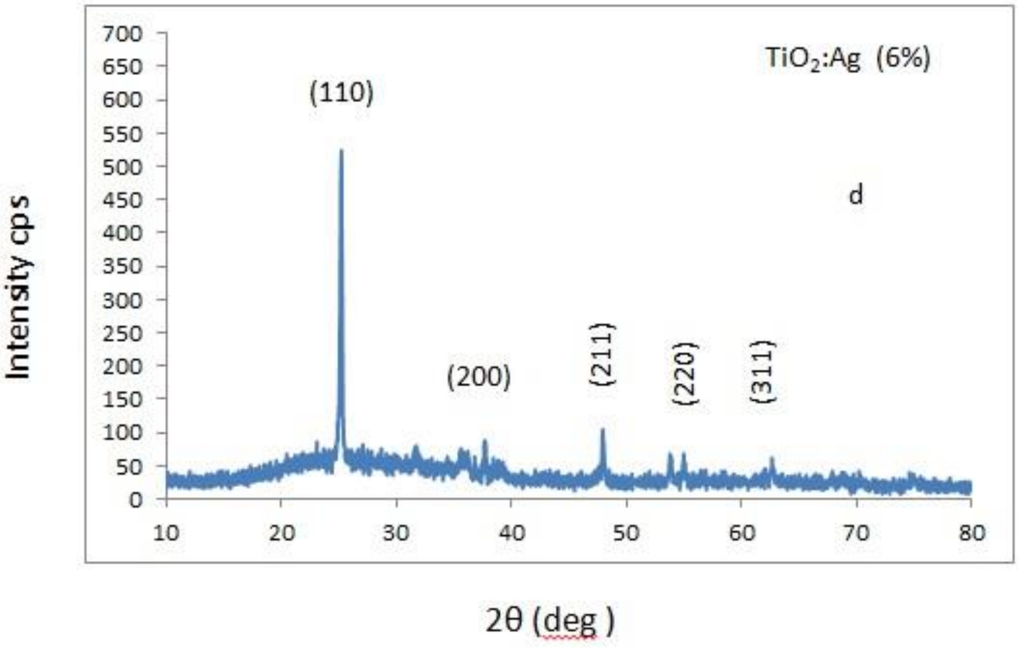


Figure (1) X-ray diffraction spectrum of (a) TiO_2 (pure) (b) TiO_2:Ag (2%) (c) TiO_2:Ag (4%) (d) TiO_2 : Ag (6%)

Table (1) X-ray diffraction results of pure and silver Ag-doped TiO_2 thin films prepared by thermochemical spraying method.

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	Std.(Å)d_{hkl}	hkl	Cs
TiO_2(Pure)	25.2492	0.19170	3.52440	3.520000	(101)	7.741
	37.7415	0.21200	2.38163	2.378000	(004)	7.216
	47.9732	0.19200	1.89485	1.892000	(200)	8.253
	53.8316	0.19000	1.70164	1.699900	(105)	8.545
	55.0094	0.19330	1.66796	1.666500	(211)	8.445
	62.6260	0.13500	1.48216	1.480800	(204)	12.555
TiO_2:Ag(2%)	25.2485	0.20220	3.52449	3.342000	(110)	7.337
	37.7378	0.17130	2.38185	2.362000	(200)	8.935
	47.9674	0.18640	1.89507	1.929100	(211)	8.500
	53.8566	0.28660	1.70091	1.670900	(220)	5.665
	54.9827	0.16670	1.66871	1.670900	(220)	9.794
	62.6141	0.15470	1.48242	1.425000	(311)	10.958
TiO_2:Ag(4%)	25.2707	0.17560	3.52145	3.342000	(110)	8.450
	37.7398	0.15140	2.38173	2.362000	(200)	10.108
	47.9872	0.16740	1.89433	1.929100	(211)	9.467

	53.8291	0.18500	1.70171	1.670900	(220)	8.778
	54.9994	0.20670	1.66824	1.670900	(220)	7.897
	62.6060	0.15500	1.48259	1.425000	(311)	10.933
TiO_2:Ag(6%)	25.2591	0.18640	3.52304	3.342000	(110)	7.962
	37.7463	0.14970	2.38133	2.363000	(200)	10.223
	47.9827	0.16200	1.89450	1.929100	(211)	9.781
	53.8449	0.22330	1.70125	1.670900	(220)	7.274
	55.0164	0.17270	1.66777	1.670900	(220)	9.455
	62.6934	0.18000	1.48073	1.425000	(311)	9.418

It has been studied the transmittance, absorption, and optical energy gap spectrum of pure TiO_2 thin films doped with silver Ag at percentages (2, 4, 6). Figure (2) shows the transmittance spectra of pure and doped (TiO_2) thin films. The optical is made by a part of the impurities, and it increases with an increase in its percentage in the thin films. By increasing the optical absorbance, the optical transmittance decreases when doping. It has been noted that the absorbance behaves opposite to the permeability as in Figure (3). Pure and dotted with silver Ag, where the energy gap values decrease as the percentage of doping increases, as in Figure (4), and this is consistent with what the researchers reached [25,24].

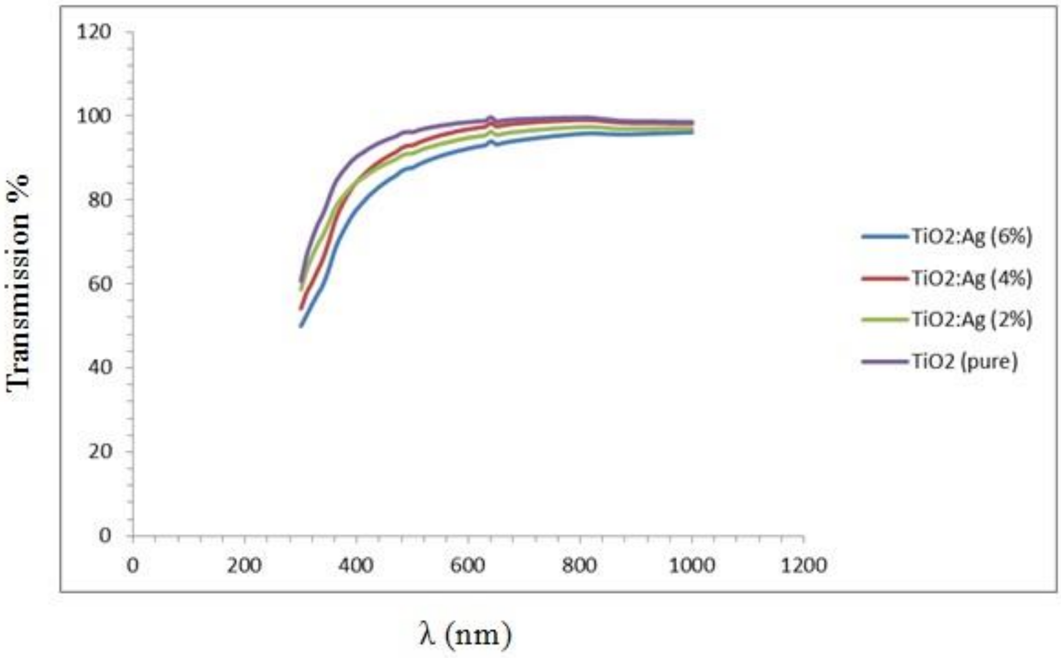


Figure (2) Transmittance spectrum as a function of the wavelength of pure titanium dioxide (TiO_2) thin films dotted with silver (Ag) in percentages of (2,4,6%)

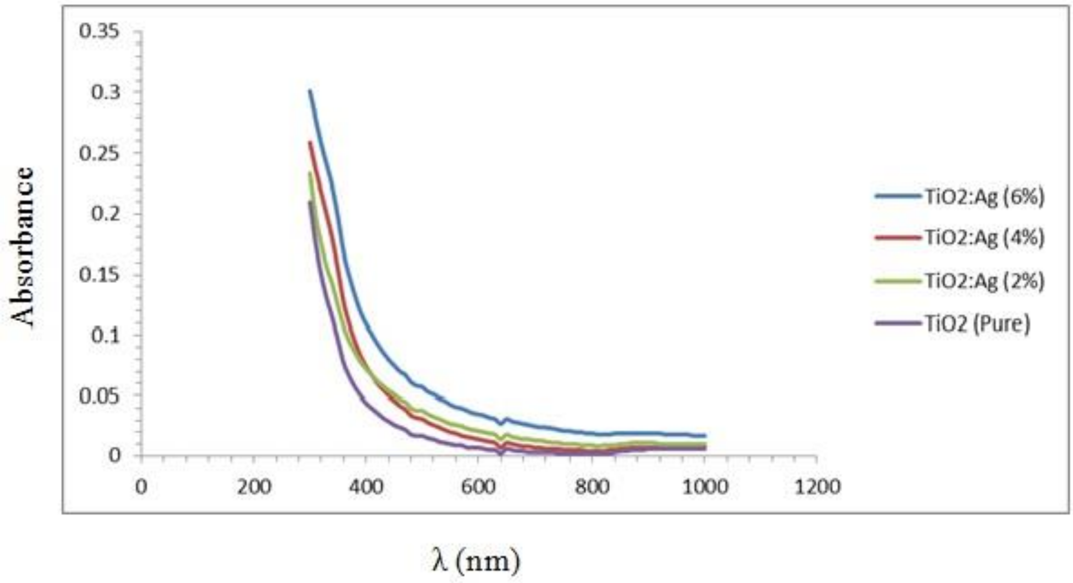


Figure (3) Absorption spectrum as a function of the wavelength of pure titanium oxide (TiO_2) thin films doped with silver (Ag) in percentages of (2,4,6%).

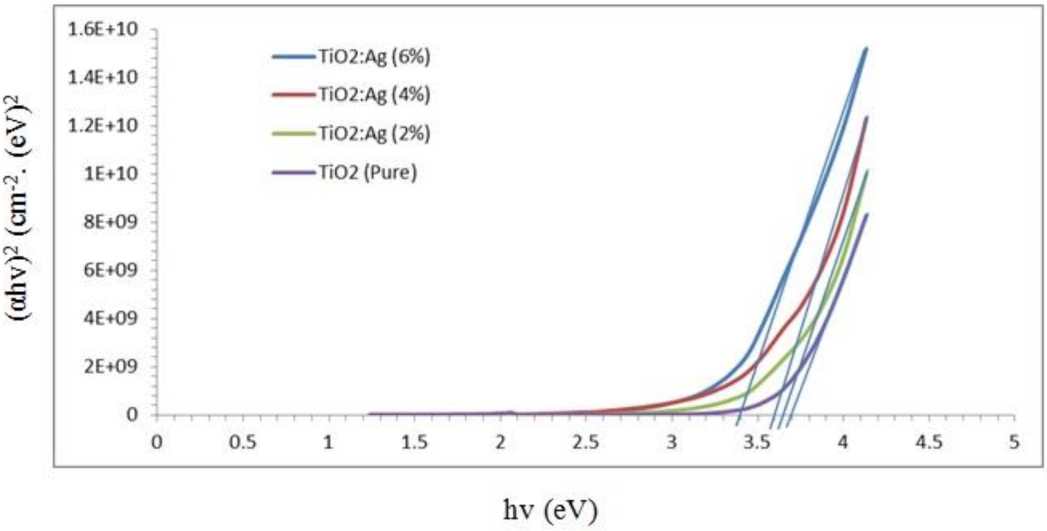


Figure (4) The values of the energy gap prohibited for direct transfers of pure titanium dioxide (TiO_2) thin films doped with silver (Ag) in percentages of (2,4,6%)

The results of the Hall effect measurements based on the relationship (1) showed that all the prepared thin films are of the negative type, through the negative sign of the Hall coefficient, and from this relationship also the concentration of the majority carriers was calculated. The results showed by relying on equation (4) that titanium dioxide TiO_2. It has a mobility value of (5.58E+03 cm2v-1s-1) at room temperature, and these results are almost in agreement with what was reached by other researchers [27,26]. As for the doping of the films, there was a clear increase in the concentration of carriers and a decrease in the mobility values at room temperature with an increase in the doping ratios as in Table (2).

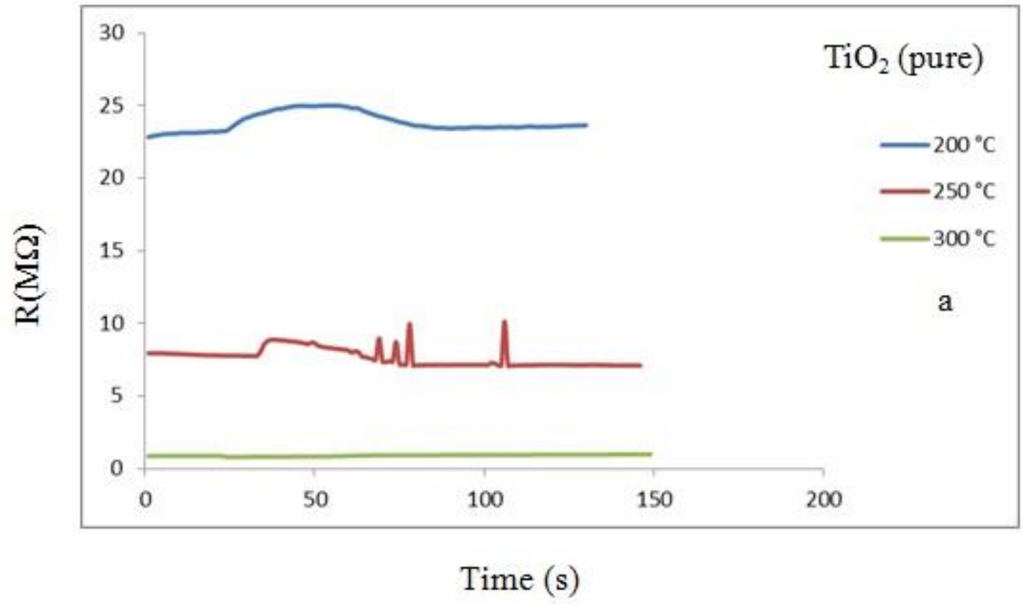
The reason for this is due to the increase in the concentration of carriers in the local levels formed near the conduction band, which in turn leads to an increase in the number of electron-donating atoms capable of ionization within a thermal energy that does not exceed a value (K_BT), as the increase of impurities leads to a decrease in the average free path time, which in turn leads To a small decrease in the value of mobility compared to the obvious increase in the concentration of electrons, and the latter is responsible for the increase in conductivity at constant temperature.

Table (2) Practical results of Hall effect calculations for the prepared thin films

Sample	n $(cm)^{-3}$	R_H $(cm^{-3}C^{-1})$	$\sigma(o.cm)^{-1}$	**μ** $(cm^2V^{-1}s^{-1})$	Type
TiO_2(pure)	2.05E+17	-3.05E+02	1.83E+01	5.58E+03	N
TiO_2:Ag 2%	1.19E+17	-5.25E+03	1.71E+01	4.75E+02	N
TiO_2:Ag 4%	2.48E+17	-9.99E+03	1.88E+01	1.71E+02	N
TiO_2:Ag 6%	6.25E+17	-2.52E+01	2.50E+01	1.31E+02	N

Allergic properties of pure titanium oxide (TiO_2) thin films studied with silver Ag with doping percentages (2, 4, 6)% and deposited on glass substrates were studied. The measurements were made using (NO_2) gas prepared in the laboratory, and the change of sensitivity of the thin films of the gas with the change of temperature, and the change of the resistance with the change of time at a certain temperature were calculated.

The electrical resistance of pure and tainted titanium oxide (TiO_2) thin films was measured as a function of time by holding the temperature constant and then measuring the resistance directly for different temperatures, when the operating temperature changed (200-300 °C). Figure (5-a) shows a change in the resistance values, as their value decreases with increasing temperatures, and this is a feature that characterizes semiconductor materials, meaning that the resistance changes inversely with changing temperatures [29,28]. The same behavior occurs when doping, as we notice from Figure (5-b,c,d) the significant decrease in the temperature resistance curve (300°C) when doping compared to temperatures from (200-250°C).


TiO$_2$ (pure)
200 °C
250 °C
300 °C
a
R(MΩ)
Time (s)
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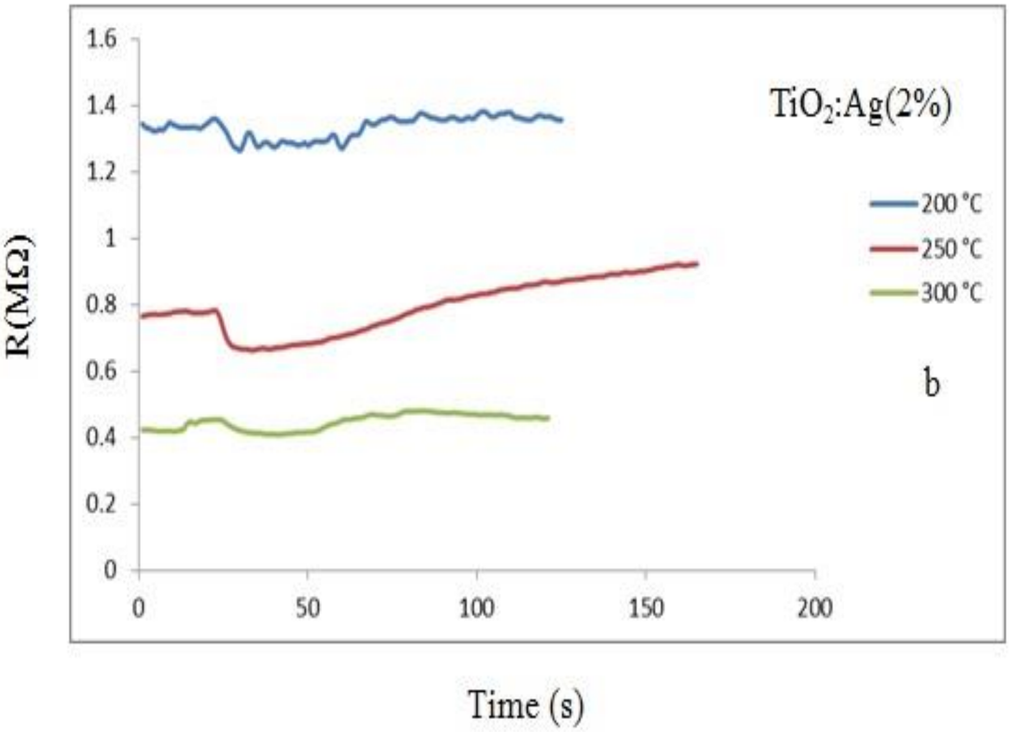
10
15
20
25
30
0
50
100
150
200


TiO$_2$:Ag(2%)
200 °C
250 °C
300 °C
b
R(MΩ)
Time (s)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
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50
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150
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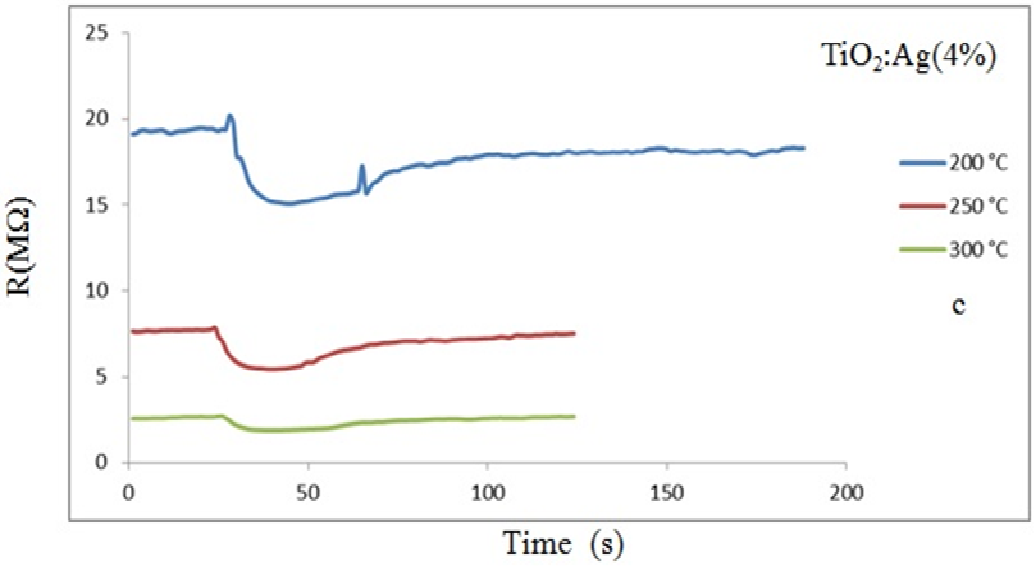


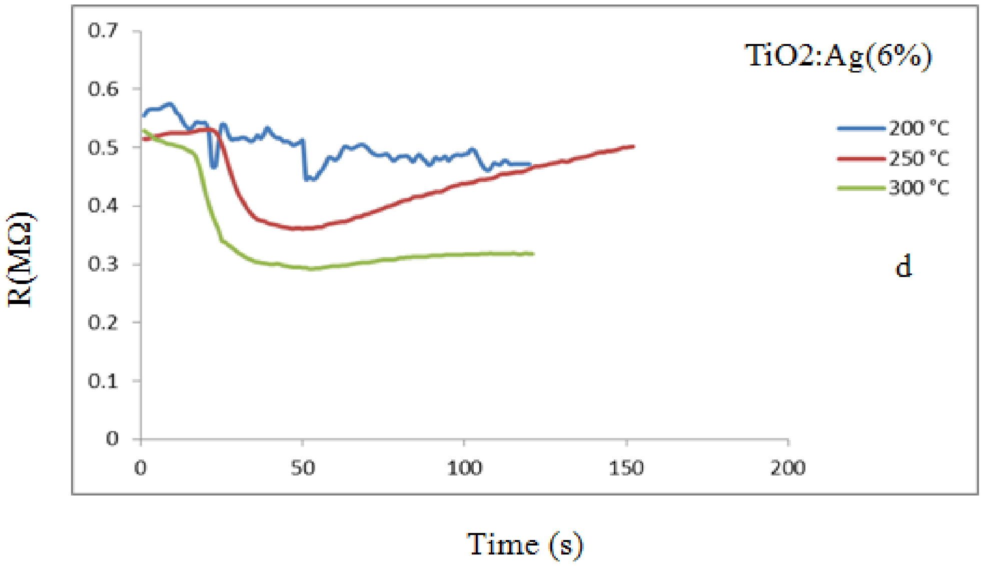
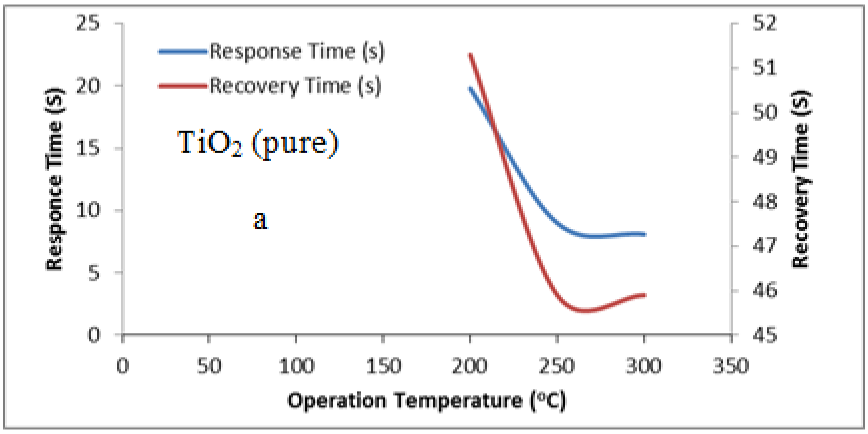


Figure (5) Resistance as a function of time at different operating temperatures for the thin films (a) TiO_2 (Pure) (b) TiO_2:Ag(2%) (c) TiO_2:Ag(4%) (d) TiO_2:Ag(6%)

In addition, the reaction time during the sensing process and the return to the initial state, which is known as the Response Time, is one of the important aspects that determine the efficiency of the sensor, as the faster the response, the higher the efficiency of the sensor at the appropriate operating temperature. Among the results we obtained, the response time was within the time range (8.1-24.3 s) for membranes on glass floors, which agree with the study [34]. As shown in Figures (6-a,b,c,d)), the data for operating temperature and response time were tabulated in Table (3).

Table (3) Operating for TiO_2 thin films temperatures of pure and doped on glass floors

Sample	T (°C)	t_{gas}(on)	t_{gas}(off)	t_{gas} recover	Response time(sec)	Recover time(sec)
TiO_2 (Pure)	200	21	43	100	19.8	51.3
	250	29	39	90	9	45.9
	300	20	29	80	8.1	45.9
TiO_2:Ag (2%)	200	21	35	110	12.6	67.5
	250	22	42	100	18	52.2
	300	21	38	90	15.3	46.8
TiO_2:Ag (4%)	200	26	42	110	14.4	61.2
	250	22	36	100	12.6	57.6
	300	24	37	100	11.7	56.7
TiO_2:Ag (6%)	200	20	47	120	24.3	65.7
	250	25	44	100	17.1	50.4
	300	21	39	80	16.2	36.9



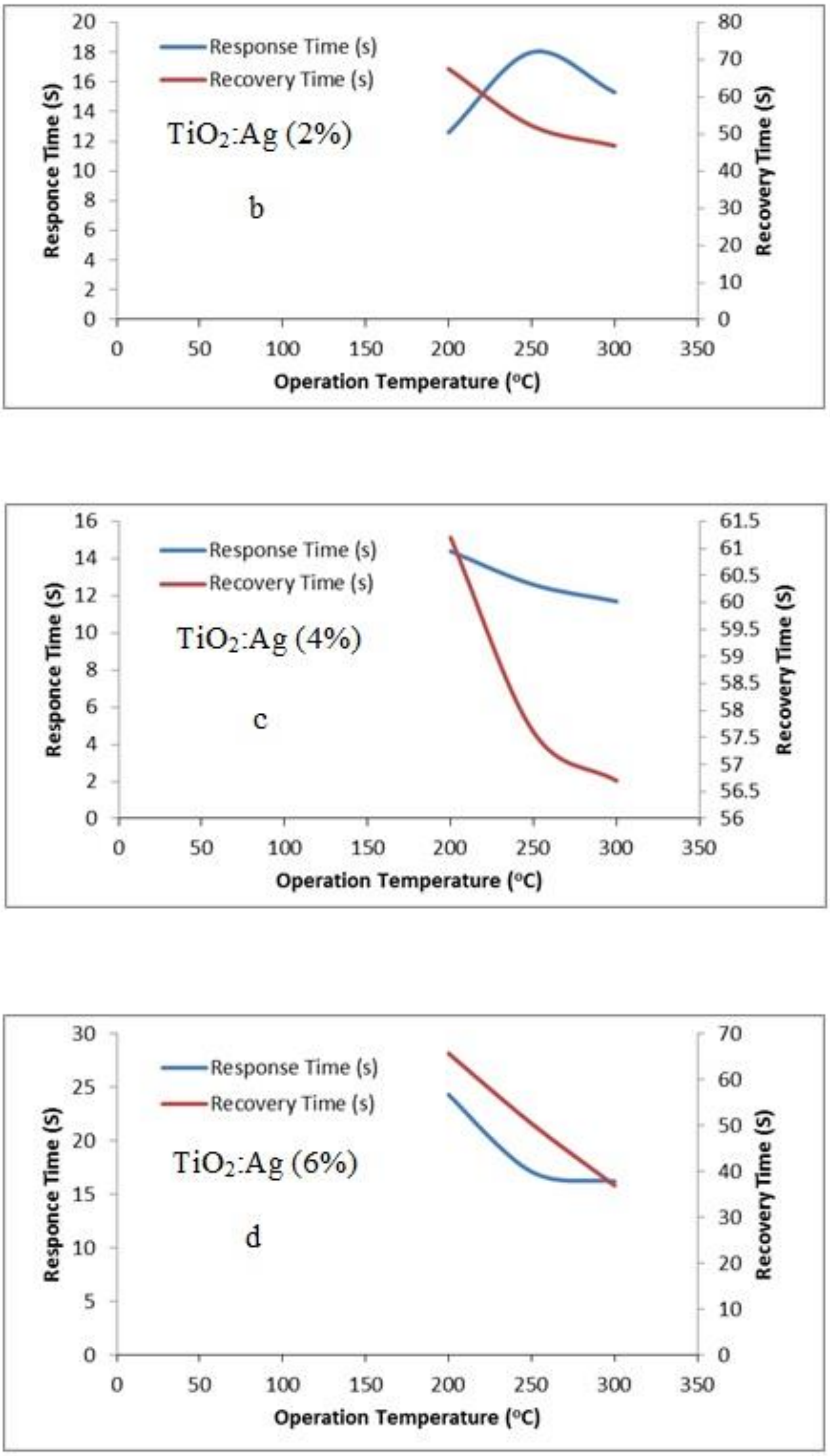


Figure (6) Response time and recovery time as a function of the operating temperature of (a) TiO_2 thin films

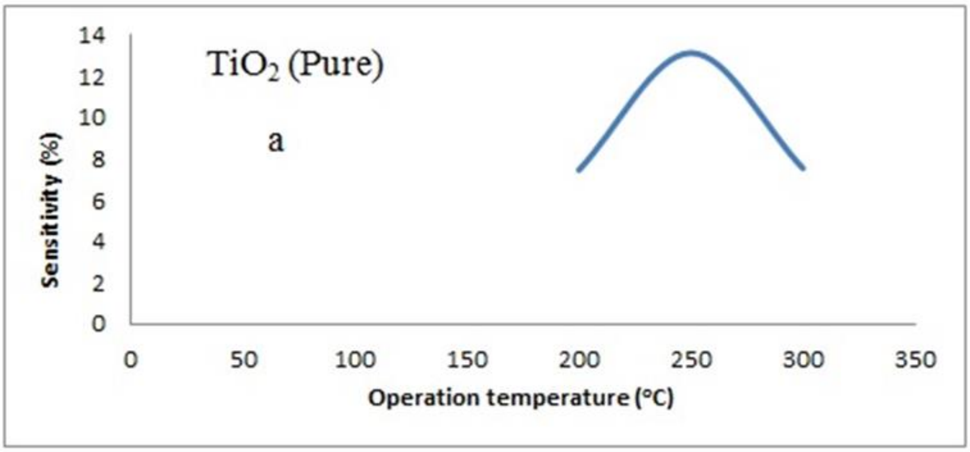
(b) TiO_2:Ag (2%), (c) TiO_2:Ag (4%), (d) TiO_2:Ag (6%)

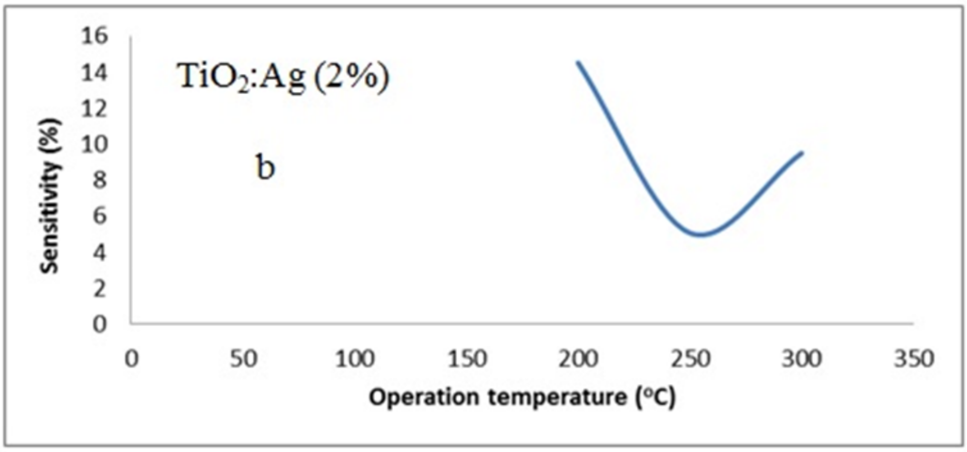
The account of sensitivity for the thin films of pure titanium dioxide TiO_2 dotted with silver Ag was calculated according to the relationship (5), where it was found that the maximum sensitivity was for titanium dioxide impregnated with silver at a rate of (6%), reaching (36.96581197) at the operating temperature (200 °C).

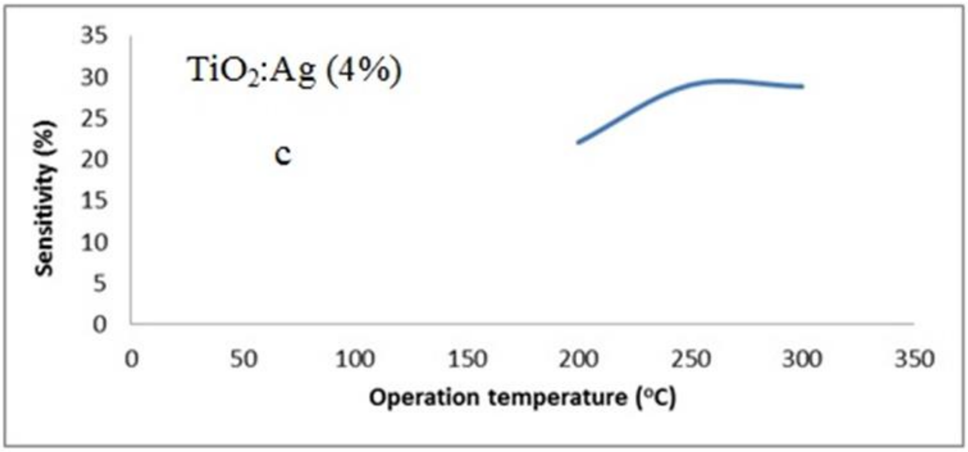
The principle of the mechanism of gas detection and adsorption mechanism that depends on the crystal structures of the thin film material so that the oxygen ions in titanium dioxide TiO_2 form a depletion layer and the growth of the voltage barrier at the granular boundaries, when the thin film is exposed to an oxidizing gas such as NO_2, the oxygen ions in titanium dioxide TiO_2 It will be absorbed by gas molecules, thus reducing the concentration of charge carriers and growing the voltage barrier to obstruct the passage of carriers as the thin film resistance increases, and this in turn leads to an increase in sensitivity [36,35]. As shown by the results listed in Table (4).

Table (4) shows the values of sensitivity and resistance (on / when gas is present, off / absence of gas) for pure and silver-doped and TiO_2 thin films deposited on glass floors

Sample	T (°C)	$R_{on}(\Omega)$	$R_{off}(\Omega)$	$S\%=(R_{on}(\Omega)-R_{off}(\Omega))/R_{on}(\Omega)*100\%$
TiO_2 (Pure)	200	23.19	24.92	7.460112117
	250	7.77	8.79	13.12741313
	300	0.888	0.821	7.545045045
TiO_2:Ag (2%)	200	0.779	0.666	14.50577664
	250	1.36	1.291	5.073529412
	300	0.453	0.41	9.492273731
TiO_2:Ag (4%)	200	19.4	15.12	22.06185567
	250	7.72	5.48	29.01554404
	300	2.667	1.898	28.83389576
TiO_2:Ag (6%)	200	0.468	0.295	36.96581197
	250	0.539	0.511	5.194805195
	300	103.7	98.5	5.014464802







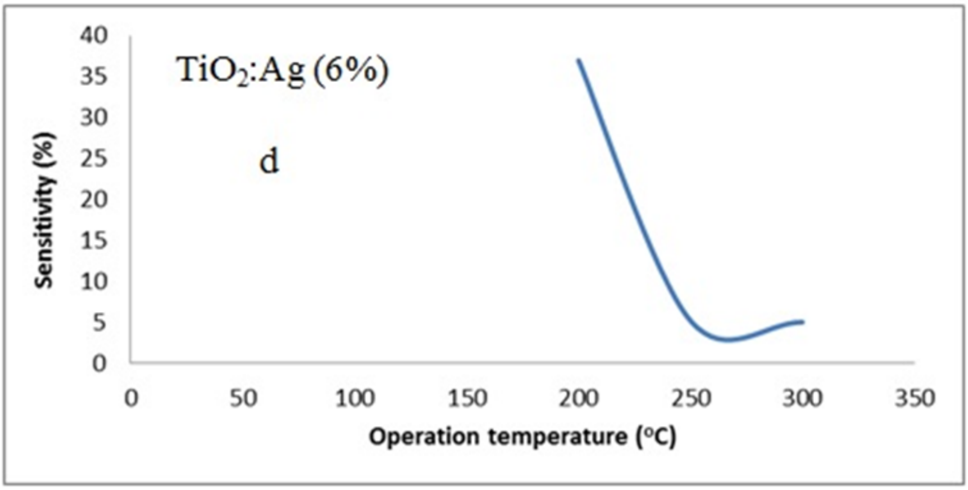


Figure (7) Sensitivity as a function of operating temperature of the thin film (a) TiO_2 (Pure) (b) TiO_2: Ag 2% (c) TiO_2:Ag 4% (d) TiO2:Ag 6%

Conclusions

The Ag-doped TiO2 membranes prepared by thermochemical spraying method have a polycrystalline structure, where we note that the dominant phase of Anatase, and the optical transmittance and energy gap of all the doped films decrease with the increase in the percentage of doping. And that the mobility values decrease with the increase in the percentage of doping and that the concentration of the carriers increases with the increase in the percentage of doping. Through the results of the sensing, we conclude that titanium dioxide impregnated with silver can be used successfully as a sensor for oxidizing and toxic gases such as NO2.

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