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Copper effect on the structural and optical properties affecting the gas sensitivity of titanium oxide nanofilms

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Summary

Thin films of pure titanium oxide (TiO2) with several copper ratios were deposited on glass substrates using an optical laser system (PLD) for pure and doping samples (TiO2 Pure, 1% Cu, 2% Cu, 3% Cu) and energy (600mj). The results of sample tests of X-ray diffraction of models have shown the appearance of four peeks of titanium oxide (200), (211), (101), (110) for angles (27.50, 36.04, 54.23, 56.78) the crystalline structure of titanium oxide films is (Tetragonal) There is a gradual decrease in the intensity of the titanium oxide peaks when the doping ratio increases, so we notice an increase in the intensity peaks of the doping material. Copper appeared in three peeks which are (111,200,220) and for the angles (43.31,50.44,74.12) and the crystalline structure of copper (Cubic). As for the optical tests, the results showed that the value of the absorption coefficient increases when the value of the optical energy gap decreases with the increase in the ratio of copper. The sensitivity properties were measured using (NO2) gas with increasing operating temperature.

Keywords

itanium oxide, copper, structural properties, atomic optical properties, gas sensitivity

Optical laser technology (PLD) depends on the deposition of a thin film as a result of the interaction between the laser and the sample material using a laser beam of high intensity. The laser system consists of three main components (laser light, sedimentation chamber, and vacuum system) [1]. A laser beam is focused on the sample, and if the laser energy is greater than the threshold energy of the sample, the material will be converted into vapor. In this way, thin films are produced [2,3]. Optical laser deposition (PLD) has achieved great success due to its low costs compared to other technologies and, it uses in many types of materials (metals, electrical insulators, semiconductors, polymers, ferroelectric, materials and, organic materials) [4]. At this time, we see that recent research is heading towards the field of transparent oxides (TCOs) because of their technological importance, and their multiple uses in solar cells, infrared detectors, and transparent transistors [5,6]. Among these oxides, titanium oxide (TiO2) is one of the important compounds because of its unique optical and electrical properties [7], so it has many uses and applications such as (microelectronic devices, electronic gates, capacitors, solar energy fields, gas sensors, paper, and plastic industry) [8,9]. Titanium oxide (TiO2) has three phases, which are Anthase (Tetragonal), Rutile (Tetragonal), and Brookite (rhombic), Rutile phase is the most stable phase, as it has the highest absorbance and the smallest energy gap (3.05eV) [10,11]. Copper is a transition metal element that rarely has a natural color other than gray or silver. Copper, in its pure state, is redorange, and when exposed to air becomes close to red [12]. Copper is characterized as a metal that has very high thermal and electrical conductivity, and it is soft, malleable, and ductile, [13,14]. Copper is used in many fields, the most important of which are as a conductor of electricity and heat, and in thermocouples to measure temperature and strain gauges, and it is the main component of many metal alloys [15]. One of the chemical properties of copper has it does not interact with water but reacts slowly with atmospheric oxygen to form a layer of black and brown copper oxide, and this layer protects the base metal from additional corrosion [16].

The practical part:

Titanium oxide powder (TiO2) with a high purity of (99.99%) was compressed, and it was doped with copper (Cu), with a purity of (98.8%)and, several doped ratios (1,2,3)%, and then the mixed powders were compressed with a pressure of (8ton) using a hydraulic press to prepare samples weighing (2) gm in the form of tablets, and then deposit them on glass substrates using PLD (Nd: YAG) optical laser system, energy (600mj), wavelength (1064nm), frequency (6Hz), distance (2cm) between the sample and the glass substrate, the number of pulses used (1000), low pressure (10^{-3} mbar), and at laboratory temperature.

Results and discussion:

X-ray diffraction results:

The results of X-ray diffraction (XRD) for pure and doped titanium oxide nanofilms showed four peaks (110), (101), (211), (200) for angles (27.50, 36.04, 54.23, 56.78). The crystalline structure of titanium oxide films was (Tetragonal). The effect of doping with copper shows a gradual decrease in the intensity of the titanium oxide peaks when the doping ratio increases and an increase in the intensity of peaks of the doping material. Copper appeared in three peaks, (111,200,220) and angles (43.31,50.44,74.12) and as shown in Table (1). The results also showed that the crystalline structure of copper (Cubic) and the width of peaks increase with the increase in the ratio of doping with copper, and leads to a decrease in the crystal size[17], so there is an inverse proportion between them according to the Shearer equation, as shown in Figure (1). The average crystal size is calculated by using (Debye-Scherrer) according to the relationship:

$D_{av} = K\lambda / \beta \cos\theta_B$ ....(1)

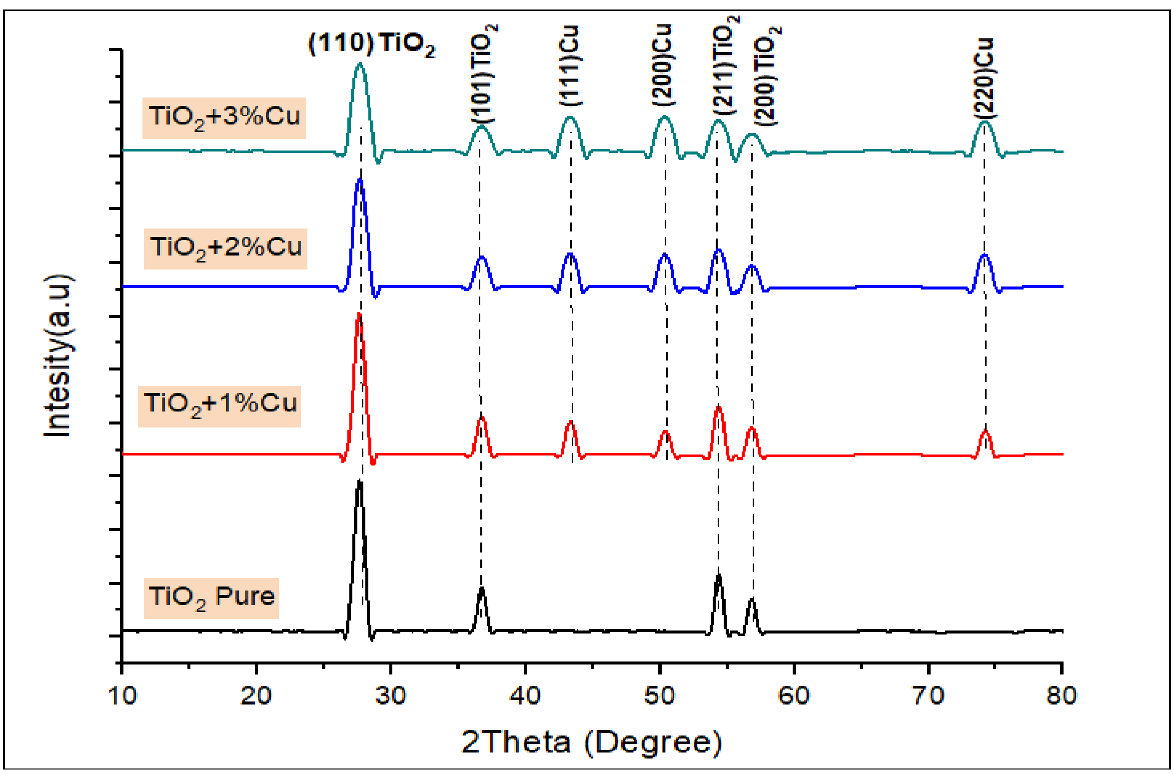

Figure (1) X-ray diffraction of titanium oxide films doped with copper

Table (1) the results of X-ray diffraction (XRD)

Card No	System	Phase	Hkl	dhkl Std (oA)	C.S (nm)	dhkl Exp (oA)	FWHM (Deg)	2Theta (Degree)	Content %
00-001-1292	Tetragonal	TiO_2	(110)	3.27	171.6787	3.24	0.49607	27.507	Pure
00-001-1292	Tetragonal	TiO_2	(101)	2.52	179.2048	2.49	0.63374	36.041	
00-001-1292	Tetragonal	TiO_2	(211)	1.72	183.8802	1.69	0.65802	54.233	
00-001-1292	Tetragonal	TiO_2	(220)	1.65	216.3348	1.62	0.78065	56.783	
00-001-1292	Tetragonal	TiO_2	(110)	3.25	171.6787	3.24	0.49607	27.507	1% Cu
00-001-1292	Tetragonal	TiO_2	(101)	2.5	149.2048	2.49	0.63374	36.041	
01-085-1326	Cubic	Cu	(111)	2.097	161.3211	2.087	0.5212	43.317	
01-085-1326	Cubic	Cu	(200)	1.817	168.4313	1.807	0.654	50.449	
00-001-1292	Tetragonal	TiO_2	(211)	1.7	153.8802	1.69	0.65802	54.233	
00-001-1292	Tetragonal	TiO_2	(220)	1.63	216.3348	1.62	0.78065	56.783	
01-085-1326	Cubic	Cu	(220)	1.09	173.4324	1.08	0.683	74.126	
00-001-1292	Tetragonal	TiO_2	(110)	3.27	178.6787	3.24	0.51607	27.507	2% Cu
00-001-1292	Tetragonal	TiO_2	(101)	2.52	156.2048	2.49	0.65374	36.041	
01-085-1326	Cubic	Cu	(111)	2.117	168.3211	2.087	0.5412	43.317	
01-085-1326	Cubic	Cu	(200)	1.837	175.4313	1.807	0.674	50.449	
00-001-1292	Tetragonal	TiO_2	(211)	1.72	160.8802	1.69	0.67802	54.233	
00-001-1292	Tetragonal	TiO_2	(220)	1.65	223.3348	1.62	0.80065	56.783	
01-085-1326	Cubic	Cu	(220)	1.11	180.4324	1.08	0.703	74.126	
00-001-1292	Tetragonal	TiO_2	(110)	3.29	187.6787	3.24	0.52607	27.507	3% Cu
00-001-1292	Tetragonal	TiO_2	(101)	2.54	165.2048	2.49	0.66374	36.041	
01-085-1326	Cubic	Cu	(111)	2.137	177.3211	2.087	0.5512	43.317	
01-085-1326	Cubic	Cu	(200)	1.857	184.4313	1.807	0.684	50.449	
00-001-1292	Tetragonal	TiO_2	(211)	1.74	169.8802	1.69	0.68802	54.233	
00-001-1292	Tetragonal	TiO_2	(220)	1.67	232.3348	1.62	0.81065	56.783	
01-085-1326	Cubic	Cu	(220)	1.13	189.4324	1.08	0.713	74.126	

Optical measurements

(1-2) Transmittance

Figure (2) shows a chart of the transmittance spectra within the wavelength range (300_1100)nm for pure and doped titanium oxide films for several ratios. Transmittance in the pure sample appeared at the highest value of more than (80%), and then gradually decreased in the transmittance spectrum of all films with an increase in copper ratios. That indicates a reverse proportion between them and is due to an increase in the thickness of the film due to increased copper ratios[18].

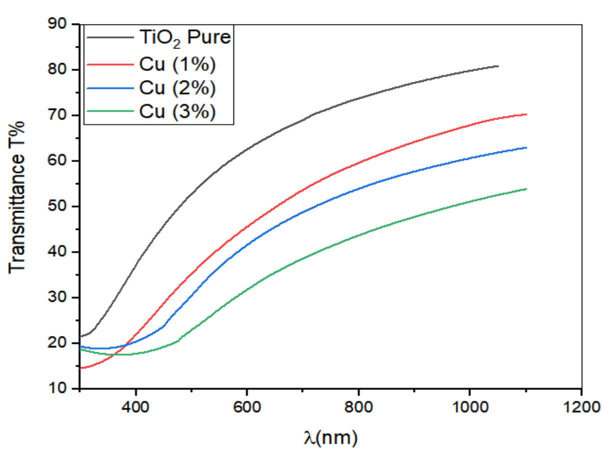

Figure (2) transmittance spectrum for pure and doped titanium oxide films

(2-2) Absorbance

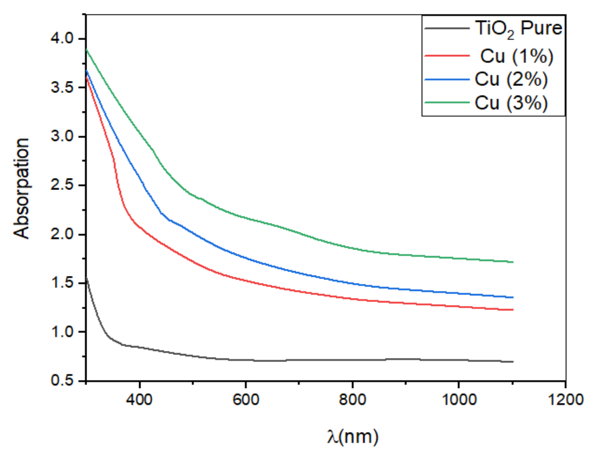

Figure (3) absorbance spectrum for pure and doped titanium oxide films

Figure (3) shows the absorption spectrum as a wavelength function, observing from the figure that absorption increases with increased doping ratios and decreases with increased wavelength (λ≥550nm). That means the absorbance is inversely proportional to the wavelength and directly with copper ratio doping, as the lowest values were obtained for the absorbance of pure titanium oxide (TiO2 Pure), and the highest values of absorbance were at doping ratios (3% Cu)[19].

(3-2) Absorption coefficient

We notice from Figure (4) that the absorption coefficient increases with the increase in doping ratios, as the highest values of the absorption coefficient were at the doping ratio (3%Cu), but the absorption coefficient decreases with wavelength because the highest absorption coefficient is at short-range wavelengths (400-550)nm because there is an inverse relationship between absorbance and permeability[20].

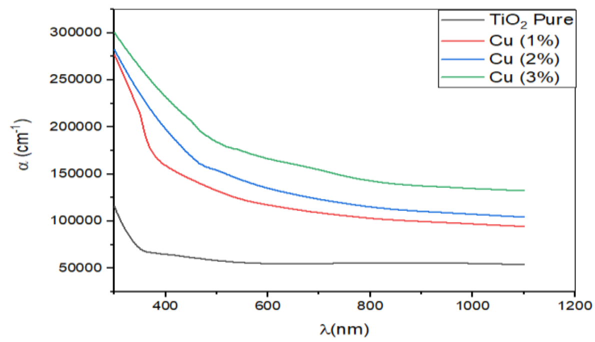

Figure (4) the absorption coefficient

(4-2) Optical energy gap

Figure (5) shows a diagram of the direct energy gaps of the films decreasing gradually with the increase in the doping ratios, as their values ranged between (2.25-3.1)eV as in Table (2), which shows all values of the optical energy gap and the energy gap for the (PL) tests. The reason for the decrease in the energy gap values is the increase in doping ratios with copper, which led to appear secondary levels between the valence band and the conduction band, which electrons were able to occupy these levels during their transition from the valence band to the conduction band[21].

Table (2) Energy gap values for titanium oxide films

Eg (eV) PL	Eg (ev)	Content %
3.23	3.1	TiO_2
2.67	0,47	1% Cu
2.51	0,26	2% Cu
2.24	0,03	3% Cu

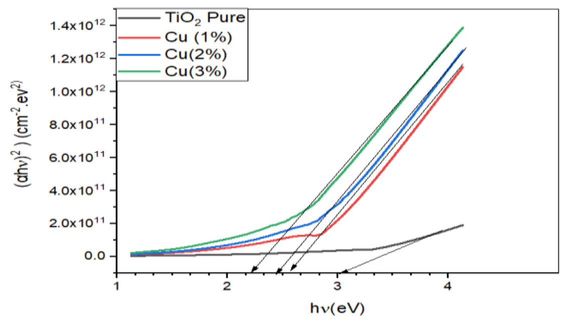

Figure (5) energy gap values for titanium oxide films

Gas sensitivity

The results of the gas sensor showed that the sensitivity of the films increases with the increase in temperature, Table (3) and Figure (6) show the sensitivity of all the films increases with the operating temperature, and the reason is due to the increase in the surface reaction rate of the film with the target gas. The highest sensitivity was found in pure (TiO2) for gas (NO2), while when the doping copper increases, we notice a decrease in the sensitivity. It is clear from that the inverse relationship between them. Table (4) with figures (7), (8), (9), and (10) show the relationship between the recovery time and the response time for all doping ratios and at the operating temperature (300 °C) and the air voltage or bias is (5V) on the glass substrates of titanium oxide films, as It is clear from the results that the pure model of titanium oxide led to a high response speed about (26 sec), while the recovery time is about (90 sec) for thin films.

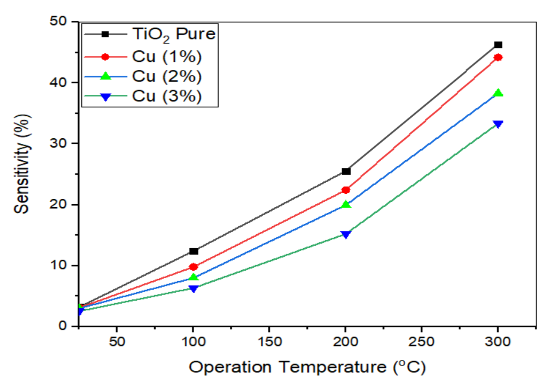

Figure (6) gas sensitivity for titanium oxide films

Table (3) the sensitivity values for all films

Operation Temperature (oC))	S % TiO2 Pure	S % Cu (1%)	S % Cu (2%)	S % Cu (3%)
25	3.20513	3.102	3.00608	2.53333
100	12.41935	9.81145	8.00278	6.33333
200	25.55403	22.43087	19.96859	15.22013
300	46.3641	44.234	38.31799	33.36353

Table (4) response and recover values.

Operation Temperature (oC)	Recover Time (sec)	Response Time (sec)	Recover Time (sec)	Response Time (sec)	Recover Time (sec)	Response Time (sec)	Response Time (sec)	Response Time (sec)
	pure	Pure	Cu (/%)	Cu (1%)	Cu (0%)	Cu (0%)	Cu (1%)	Cu (1%)
25	90.9	26.1	65.3	25.8	63.3	24.7	62.1	23.9
100	65.7	24.3	63.3	25.4	60.9	23.1	58.1	22.1
200	46.8	22.5	44.9	23.3	43.4	21.6	42.2	20.1
300	46.8	22.3	45.3	21.2	36.3	19.7	33.4	19.3

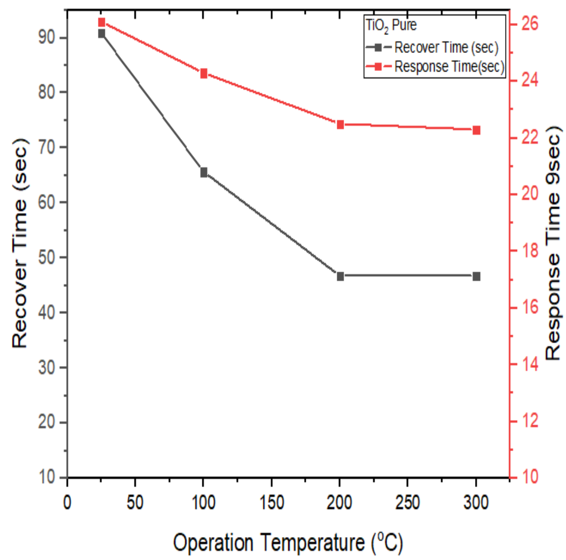

Figure (7) response time and recovery time of pure titanium oxide films

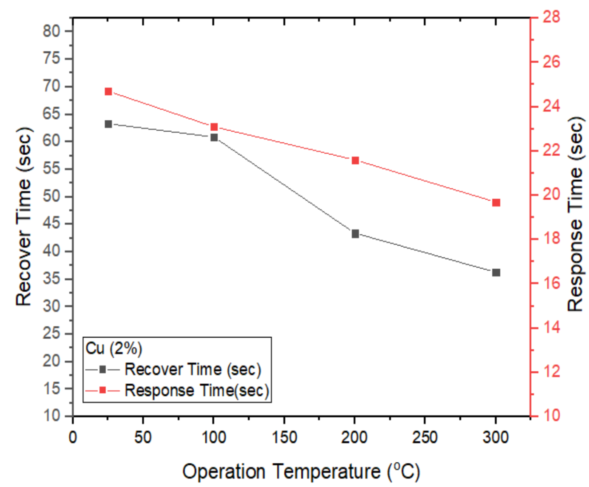

Figure (9) response time and recovery time of titanium oxide films doping (2%Cu)

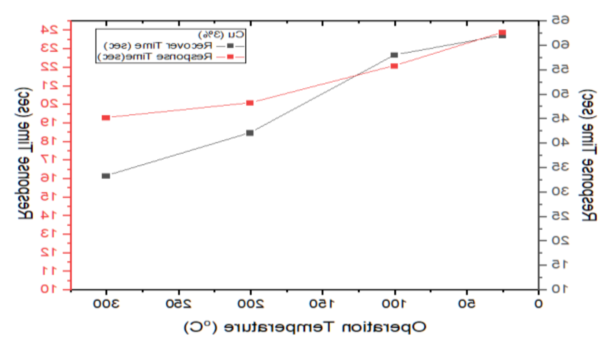

Figure (10) response time and recovery time of titanium oxide films doping (3%Cu)

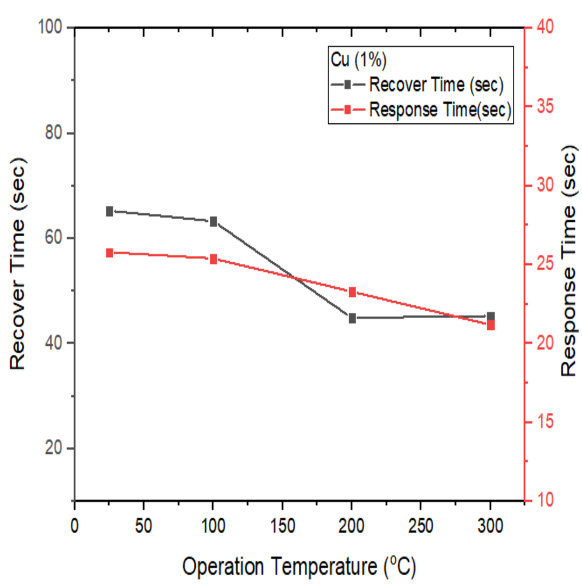

Figure (8) response time and recovery time of titanium oxide films doping (1%Cu)

Conclusion

1- The X-ray test showed that the doping leads to a gradual decrease in the intensity of the titanium oxide peaks when the doping ratio increases, and an increase in the intensity of the copper peaks.
2- The absorption coefficient increased when the doping ratio increased, as the highest value of the

absorption coefficient was at the doping ratio (3%Cu).

3- Decrease in the value of the optical energy gap when increasing the doping as a result of increasing the thickness of the film, which leads to an increase in the absorbance

4- When the doping ratio increases, we notice a decrease in sensitivity. It is clear from the relationship is inverse between them.

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