Study of Structural , Optical and Electrical Properties for Cr -Doped Tio_2 Sensor for NH_3 Gas

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ABSTRACT

Titanium doxide (TiO_2) thin films were deposited on quartz substrates by spray pyrolysis method using titanium tetrachloride as precursor solution. Thin films were deposited at temperature substrate 350 ◦C and annealed at 550 ◦C in air for 120 min. Polycrystalline thin films with anatas crystal structure, as evidenced from X-ray diffraction pattern. Optical study shows the optical band gap has been increased with increasing of dopant. Electrical properties have been studied by means of electrical resistivity and Hall measurement. The sensitivity of TiO_2: 5% Cr to NH3 gas with concentration 5ppm at room temperature has been modified to (93) % as compared with a pure TiO2.

Keywords: Thin films; Spray pyroi lysis, Doping ,Optical properties

دراسة الخصائص التركيبية والبصرية والكهربائية لمتحسس ثنائي اوكسيد التيتانيوم المشوبة بالكروم لغاز الامونيا

الخلاصة

في هذا البحث تم ترسيب ثنائي اوكسيد التيتانيوم الرقيقة على قواعد من كوارتز بطريقة الرش الكيميائي باستخدام محلول رباعي كلوريد التيتانيوم . حيث كانت درجة حرارة القاعدة 350ºC ولدن عند حرارة 550 ºC لمدة 120 min في الهواء . بينت حيود الاشعة السينية ان الاغشية متعددة البلورية مع طور الاناتاس . اظهرت دراسة البصرية ان فجوة الطاقة البصرية تزداد بزيادة نسبة التشويب .درست الخصائص الكهربائية بواسطة المقاومة الكهربائية وقياسات هول. تم حساب التحسسية لغاز NH_3 تحت تركيز (5) جزء لكل مليون . امتلك اوكسيد التيتانيوم المشوب بنسبة تركيز 5٪ من الكروم تحسسيه اكبر من اوكسيد التيتانيوم النقي وكانت 93 ٪.

INTRODUCTION

Over the last few years, interest in titanium dioxide (titania, TiO_2) has increased rapidly and significantly due to the material's potential applications in photovoltaics and photocatalytic processes[1].Titanium dioxid(TiO_2) (titania) is a cheap, excellent chemical stability, high refractive index, nontoxicity, good mechanical properties and one of the most efficient semiconductor photocatalysts for extensive environmental applications because of its strong oxidizing power, high photochemical corrosive resistance and cost effectiveness[2,3]. There are three different phases for titanium dioxide: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic)[4]. In general, anatase films are known to

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have high transparencies (allowing coatings on glass and solar cells) and small grain sizes (providing higher surface areas for photocatalysis)[5,6]. However, anatase is a wide band gap semiconductor (3.2-3.5 eV) and rutile films have band gaps (3.0-3.2 ev) [7 ,8]. Rutile has a high values of refractive index (2.7) and dielectric constant. Brookite has been rarely used because its preparation is quite difficult [9]. Anatase possesses a higher photocatalytic activity than rutile due to the difference in the optical band gap[10].There are many techniques to synthesis TiO_2 thin films, including sol–gel ,sputtering , anodic oxidation, pulsed laser deposition (PLD) , electron-beam evaporation and spray pyrolysis [8]. Among available techniques Spray pyrolysis is a cheap chemical deposition procedure, allowing the growth of rough-surface films at atmospheric pressure and on large area[11].
In this paper, effects of doping on the Structural , optical and electrical properties of spray-deposited TiO_2 thin films are discussed.

Experimental part
Undoped and chromium-doped titanium oxide thin films were deposited on heated quartz substrates (350℃).The TiO_2 films (undoped)are prepare by using a solution of (0.5 ml) titanium tetrachloride ($TiCl_4$) dissolved in (5 ml) absolute ethyl alcohol (96%). The salt[CrO_3] are used to dope TiO_2 film at different percentages (1,2,3,4 and 5%) for dopant. The method involves spraying of a desired titanium precursor through an atomizer onto preheated substrates maintained at suitable temperature. The properties of spray-deposited TiO_2 thin films were found to be dependent on the processing conditions and precursors.A Cecile CE 7200 Spectrophotometer supplied by Aquarius company wasused to record the optical transmission for TiO_2/quartz thin films for the range (300-1100 nm).The data from transmission spectrum can be used in the calculation of extinction coefficient (K),absorption coefficient(α) and band gap for TiO_2 films.X-ray diffraction measured have been performed in standart 2θ configuration with aShimadZU600 diffractometer (CuKα radiation ,40KV,30Ma). titanium tetrachloride ($TiCl_4$, purity 99.9% , 189.71 gm/mol, 1.726 g/ cm^3 density) which are made in"England" and prepare after cooling.

Structural Properties
X-Ray Diffraction
TiO_2 films pure and doped with (Cr) at different doping concentration (1,2,3,4 and 5 %) deposited on quartz substrate and annealed at temperature(550ºC) for (120min) are shown in figure (1). It is found that all the films are polycrystalline with a tetragonal crystal structure. All films show diffraction peaks belong to anatase A(101),A(004) and A(200) . The diffraction peaks are in good agreement with those given in JCPD data card (JCPDS no .21-1272) for anatanse phase .The decrease in intensity of peak (101)with increasing the dopping content and increase in full-width at half- maximum (FWHM) means decrease in grain size of film . The doped films become less crystalline than undoped sample . The peaks in the X- ray diffraction shift into the region of higher 2θ, indicating stress in the grains. XRD analysis also did not detect the dopant phase, these due to the low concentration of dopants of TiO_2 :Cr at different doping concentration on the films structure are given in table (1). The lattice parameters (a, c) can be calculated using the relations[12]:

$$a = b = 2 * d_{200} \quad \ldots(1)$$

$$c = 4 * d_{004} \quad \ldots(2)$$

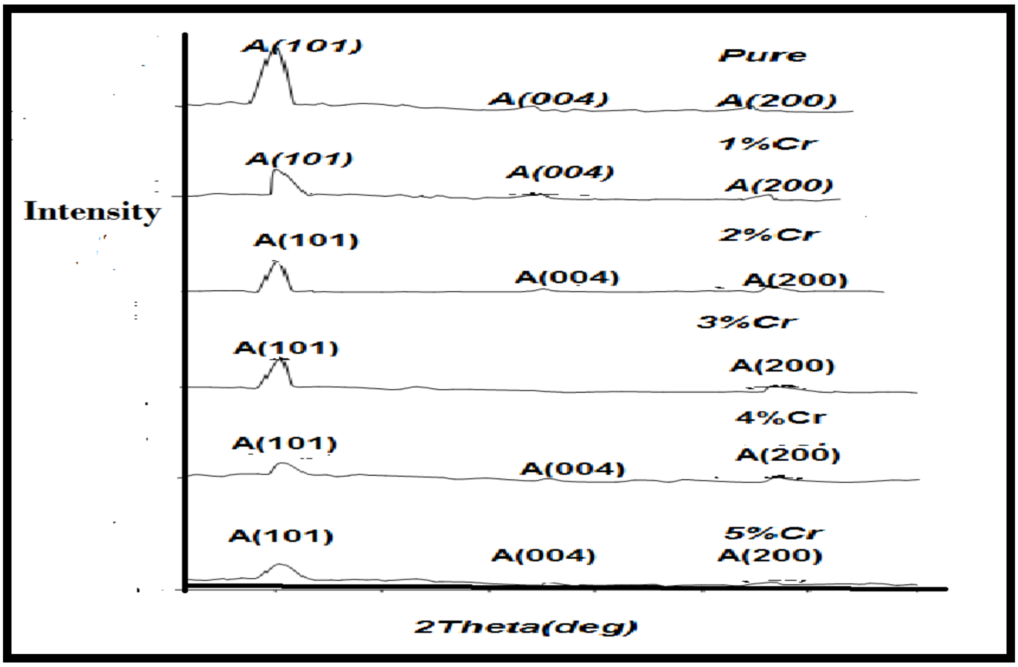

Figure. (1) XRD patterns of TiO_2 films pure and doping with chromium at different concentration.

Table(1): Experimental results for Undoped TiO_2 and doping with different doping concentration.

TiO_2 doping with Chromium	2(θ) deg	hkl	β (deg)	Grian size (nm)	a=b (nm)	c (nm)	c/a
Undoped TiO_2	25.27	A(101)	0.272	29.87	0.37914	0.958989	2.52
1% Cr	25.2	A(101)	0.4900	16.624	0.378518	0.958976	2.533
2% Cr	25.21	A(101)	0.5200	15.676	0.3766712	0.955844	2.537
3% Cr	25.32	A(101)	0.53410	15.259	0.37664	0.950068	2.522
4% Cr	25.26	A(101)	0.54170	15.029	0.37389	0.944	2.524
5% Cr	25.305	A(101)	0.54694	14.302	0.37024	0.9804	2.533

Optical properties

Transmission

Figure(2) show the optical transmission spectrum for the undoped and doped samples. For all the films, high transmission shown at long wavelengths ,the chromium-doped sample records the high transmittance across the considered spectrum. . The effect of doping on the transmission of TiO_2 films can be linked with decreasing in partical size.

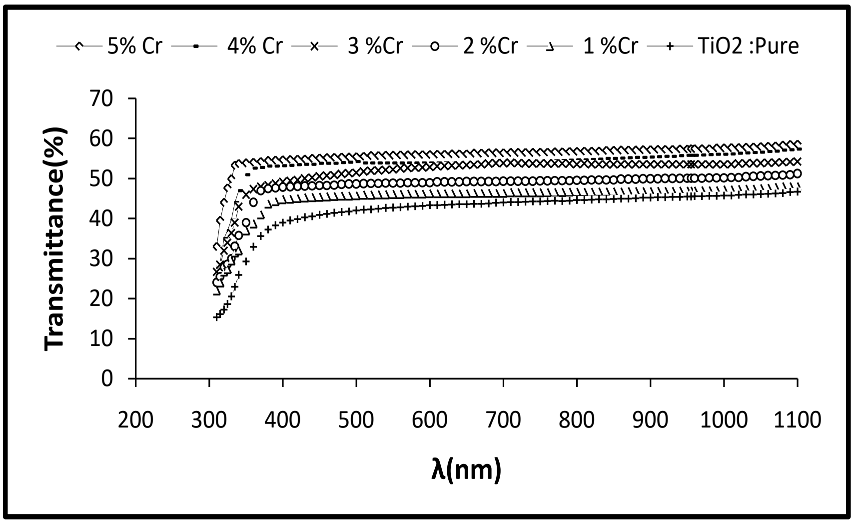

Figure (2) Transmittance spectra of TiO_2 thin films pure and doping with chromium.

Extinction coefficient

Figure (3) shows the influence of TiO_2 doping with(Cr) at different doping concentration (1,2, 3,4 and 5 %) deposited on quartz substrate at annealing temperature(550ºC) for (120min) on the extinction coefficient . It is found that extinction coefficient decrease with increasing doping concentration due to the decrease in the absorption .

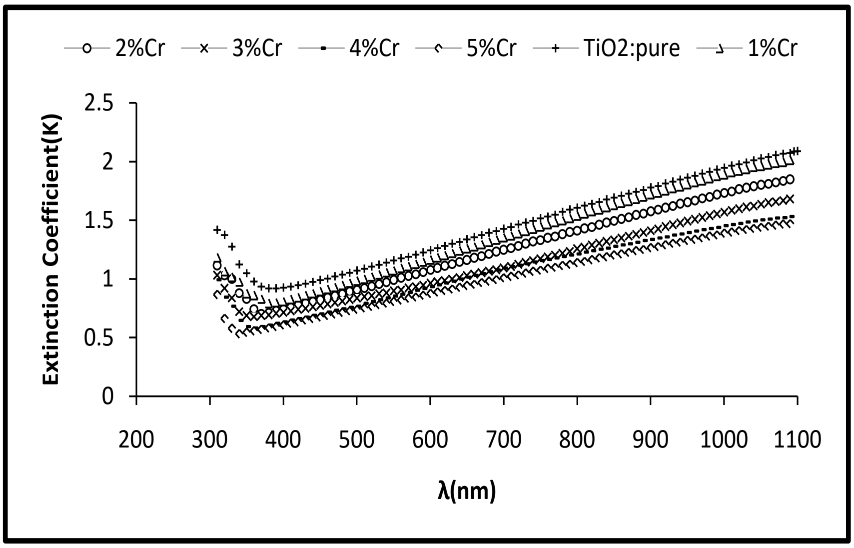

Figure (3) Variation of extinction coefficient(K) versus wavelength (λ) for pure and doping TiO_2 .

The absorption coefficient

Figures (4) show the absorption coefficient (α) of the TiO_2 thin films (at annealing temperature in 550ºC for 120 min) with different doping concentration. The absorption coefficient of TiO_2 thin films is decreased in visible region and increase doping concentration of the films.

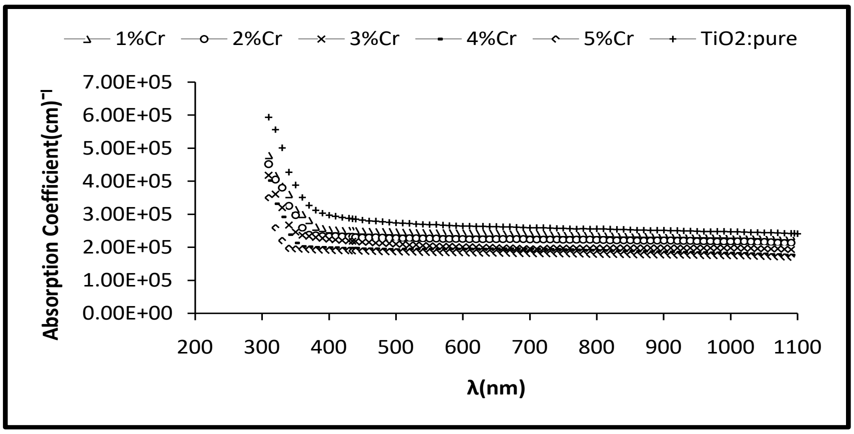

Figure (4): The optical absorption coefficient as a function of wavelength for pure

Band Gap

Figure (5) shows a plot of $(\alpha h\nu)^2$ versus($h\nu$) for TiO_2 films at different doping concentration (1,2,3,4 and 5 %). The results show decrease in energy gap with increase doping concentration of (Cr) in TiO_2 films . we could attributed this to defects increases with decrease in grain size (become less crystallinity as is evident from the X – ray diffraction) . Also This reduction in band gap is as a result of impurity states which introduce tail energy levels either in the conduction band or valence band of the titanium dioxide.

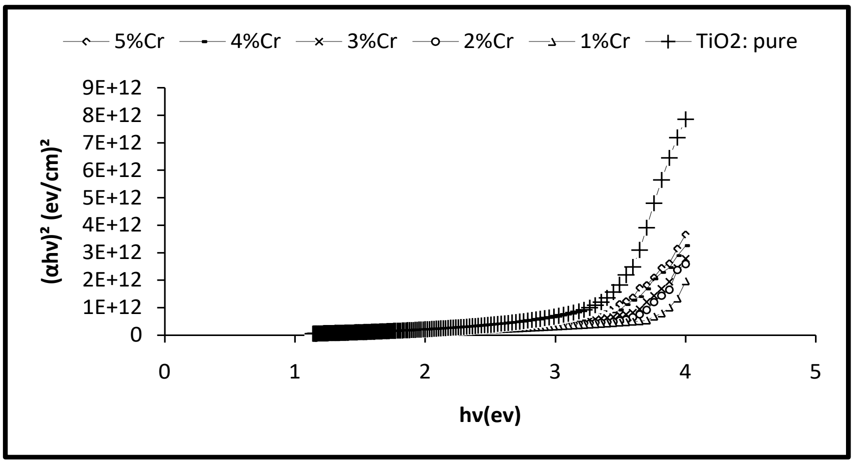

Figure (5):Aplots of $(\alpha h\upsilon)^2$ verses(hυ) of TiO_2 in films at different doping concentration and pure.

Electrical properties

Resistivity

In order to investigate the effect of chromium doping on some electrical properties of TiO_2 films, electrical resistivity as a function of doping concentration(Cr)was drawn in figure (6). The figure show that the electrical resistivity decreases with increasing doping concentration(Cr) in TiO_2 thin films.This could be attributed to the decrease of the average grain size (as shown by X- ray diffraction).

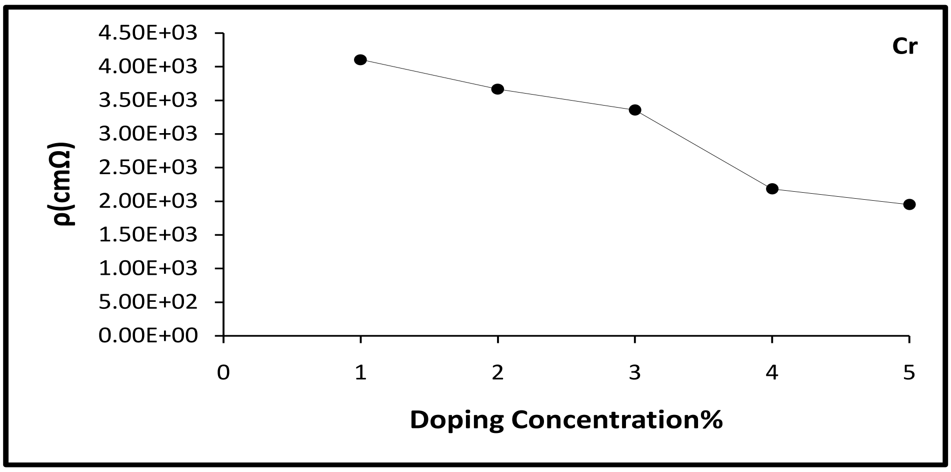

Figure (6): The electrical resistivity as a function of different doping concentration with chromium.

Hall Measurment

The results obtained from Hall effect forCr doping TiO_2 and pure were (n-type). The results have shown that a greater increase in the value of electrical conductivity, accompanied by a clear increase in the values of charge carriers with the decrease in the values of both the mobility and Hall coefficient. The value of (R_H) decreases with the increasing of doping concentration in the films as shown in table (2). Hall coefficient sign has not been changed by the increase in doping concentration . Which indicates that the electrons are the charge carriers and are responsible for the increased conductivity, as shown in table (2). The mobility decrease with increasing doping concentration in TiO_2thin films .The results may be attributed to the average grain size decreasing with increasing doping concentration in the films (as shown by X- ray diffraction).

Table(2):The obtain results of Hall measurement for TiO_2 doping with Chromium.

Samples	R_H (cm^3/C)	Carrier type	n$(cm)^{-3}$	μ_H (cm^2/v.s)
pure	-4.996	n	$1.250*10^{17}$	5.198
1%Cr:TiO_2	-6.049	n	$1.032*10^{18}$	$1.184*10^{-1}$
2% Cr:TiO_2	-1.160	n	$5.381*10^{18}$	$8.776*10^{-1}$
3% Cr:TiO_2	-0. 3321	n	$7.880*10^{18}$	$5.916*10^{-1}$
4% Cr:TiO_2	-0. 1158	n	$1.501*10^{19}$	$4.773*10^{-1}$
5% Cr:TiO_2	- 0.04556	n	$2.370*10^{19}$	$5.809*10^{-2}$

Sensing Properties

In this work, the sensing properties for NH_3 gas by pure TiO_2 and doped TiO_2 were investigated as a function of time operation . Thes films have been grown on silicon (P-type)substrates by spray pyrolysis technique .The time dependence on sensitivity of different TiO_2 thin films specimens for chemical sensing using was found out NH3 gas. ammonia gas(NH3) of concentration (5 ppm).

Operation Time Effect on Resistance Properties

Figure (7) shows the resistance as function of time operation of pure TiO_2 and doped TiO_2 with chromium(Cr). Change in resistance are shown with time. The resistance of pure TiO_2 films and doped varies with (Cr) in different concentrations (1 % , 3% and 5%) . The resistance decreases with increasing doping concentrations due to increase in the sensing of the TiO_2 films**.** A minimum resistance is of TiO_2 doped with (5%) chromium . The resistance decreases drastically during the gas exposure, a maximum resistance started to increase in TiO_2 pure.

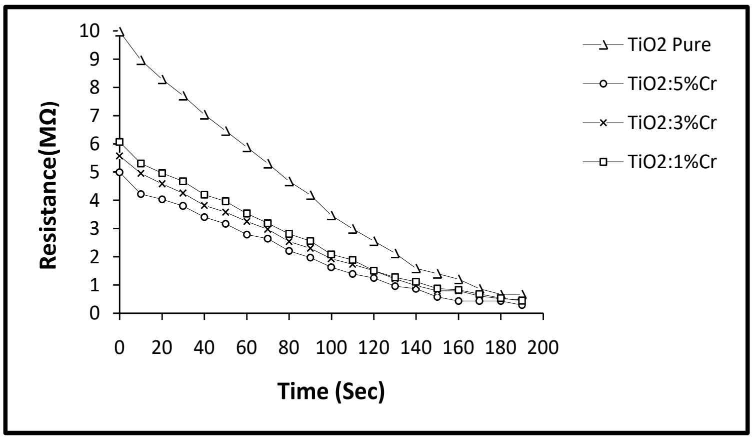

Figure (7) :Resistance of TiO_2 pure and doped with chromium as a function of operation time for NH_3 gas .

Operation Time Effect on Sensing Properties

The gas sensitivity of undoped and doped TiO_2 films is calculated from measuring the resistance change in thin films in air and in gas . Figure (8) shows the gas sensitivity of undoped TiO_2 and doped with (Chromium) . It can be seen from this observation that the sensitivity values of all samples increase with time. The sensitivity of the metal oxide semiconductor sensor is mainly determined by the interaction between the target gas and the surface of the sensor. The greater surface area of the materials stronger interaction becomes between the adsorbed gases and the sensor surface, higher gas sensing sensitivity.The sensitivity value of pure TiO_2 is less than sensitivity of doped TiO_2 because the surface species and trapped electrons are returned to the conduction band causing an increase in the conductivity of the TiO_2 films doped with respectively chromium and the sensitivity of the sensor increases.

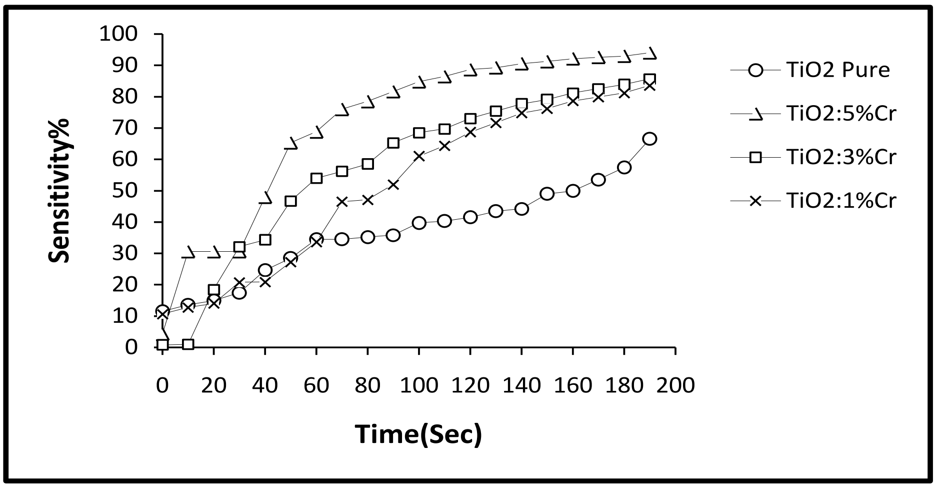

Figure (8) :Sensitivity of TiO_2 pure and doped with chromium, films for NH_3 gas at different operation times.

Conclusion

Titanium oxide thin films (undoped and Cr-doped) were fabricated by spray pyrolysis. From XRD results it is found that all the films are polycrystalline with a tetragonal crystal structure. The structure of TiO_2 doping with (Cr) thin films became less crystalline than undoped sample.

With the increase in dopant concentration to 5 %, the average crystallite size decreases. Optical studies show. The films had high transmittance in visible spectra range and the decrease in energy gap with increase doping concentration of Cr in TiO_2 films. Hall measurement indicate that the TiO_2 doping with Cr thin films have same conduction type (n-type) conductivity. The sensor TiO2 doped with Cr shows good sensitivity to NH_3 gas.

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