

Study of Structural , Optical and Electrical Properties for Cr -Doped TiO₂ Sensor for NH₃ Gas

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ABSTRACT

Titanium dioxide (TiO₂) 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 anatase 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 TiO₂: 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 pyrolysis, 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 350°C ولدن عند حرارة 550 °C لمدة 120 min في الهواء . بينت حيود الاشعة السينية ان الاغشية متعدد 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 NH₃ 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, TiO₂) has increased rapidly and significantly due to the material's potential applications in photovoltaics and photocatalytic processes[1]. Titanium dioxide (TiO₂) (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 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 TiO₂ 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 TiO₂ thin films are discussed.

Experimental part

Undoped and chromium-doped titanium oxide thin films were deposited on heated quartz substrates (350 °C). The TiO₂ films (undoped) are prepared by using a solution of (0.5 ml) titanium tetrachloride (TiCl₄) dissolved in (5 ml) absolute ethyl alcohol (96%). The salt [CrO₃] are used to dope TiO₂ 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 TiO₂ thin films were found to be dependent on the processing conditions and precursors. A Cecil CE 7200 Spectrophotometer supplied by Aquarius company was used to record the optical transmission for TiO₂/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 TiO₂ films. X-ray diffraction measured have been performed in standard 2θ configuration with a Shimadzu 600 diffractometer (CuKα radiation, 40KV, 30Ma). titanium tetrachloride (TiCl₄, purity 99.9%, 189.71 gm/mol, 1.726 g/cm³ density) which are made in "England" and prepared after cooling.

Structural Properties

X-Ray Diffraction

TiO₂ films pure and doped with (Cr) at different doping concentration (1,2,3,4 and 5%) deposited on quartz substrate and annealed at temperature (550°C) 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 anatase phase. The decrease in intensity of peak (101) with increasing the doping 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 TiO₂: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]:

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

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

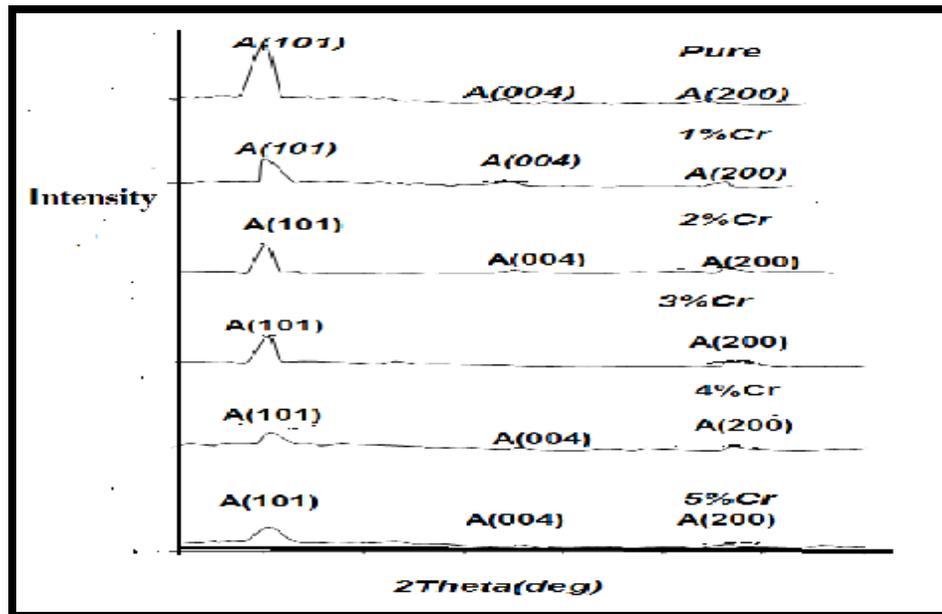


Figure. (1) XRD patterns of TiO₂ films pure and doping with chromium at different concentration.

Table(1): Experimental results for Undoped TiO₂ 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 TiO₂ films can be linked with decreasing in partical size.

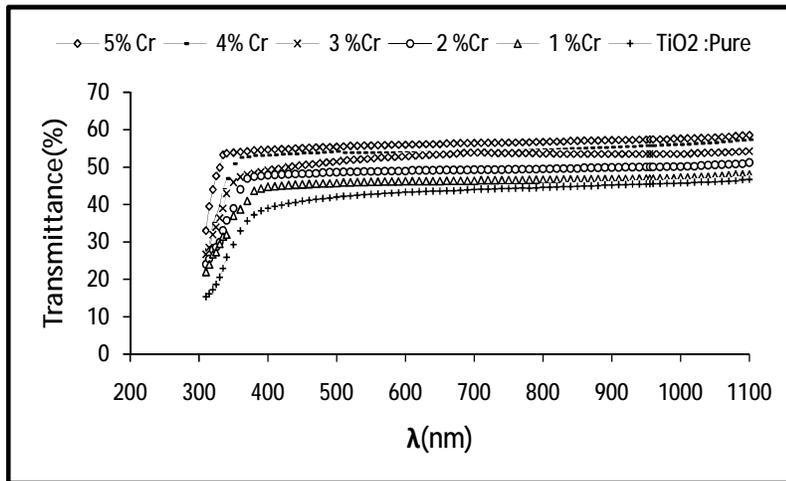


Figure (2) Transmittance spectra of TiO₂ thin films pure and doping with chromium.

Extinction coefficient

Figure (3) shows the influence of TiO₂ doping with(Cr) at different doping concentration (1,2, 3,4 and 5 %) deposited on quartz substrate at annealing temperature(550°C) for (120min) on the extinction coefficient . It is found that extinction coefficient decrease with increasing doping concentration due to the decrease in the absorption .

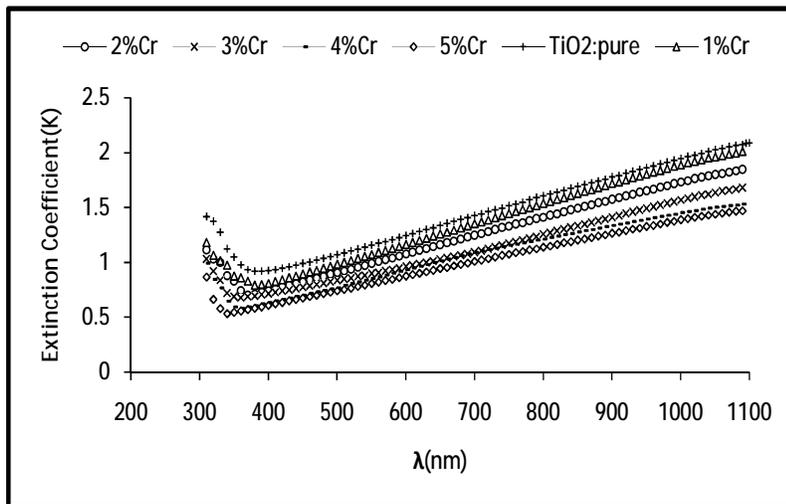


Figure (3) Variation of extinction coefficient(K) versus wavelength (λ) for pure and doping TiO₂.

The absorption coefficient

Figures (4) show the absorption coefficient (α) of the TiO₂ thin films (at annealing temperature in 550°C for 120 min) with different doping concentration. The absorption coefficient of TiO₂ thin films is decreased in visible region and increase doping concentration of the films.

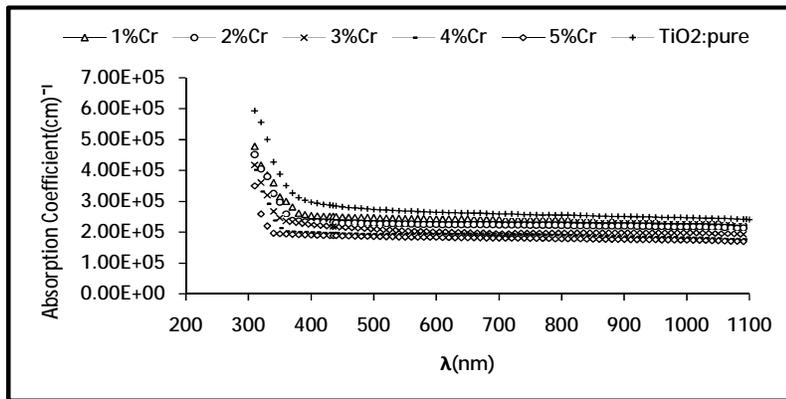


Figure (4) : The optical absorption coefficient as a function of wavelength for pure

Band Gap

Figure (5) shows a plot of $(ahv)^2$ versus (hv) for TiO₂ 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 TiO₂ 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.

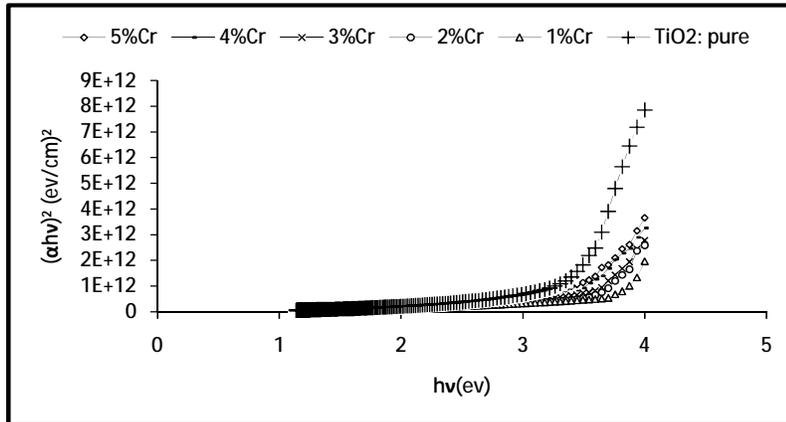


Figure (5) : Aplots of $(ahv)^2$ verses (hv) of TiO₂ in films at different doping concentration and pure.

Electrical properties

Resistivity

In order to investigate the effect of chromium doping on some electrical properties of TiO₂ 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 TiO₂ thin films. This could be attributed to the decrease of the average grain size (as shown by X- ray diffraction).

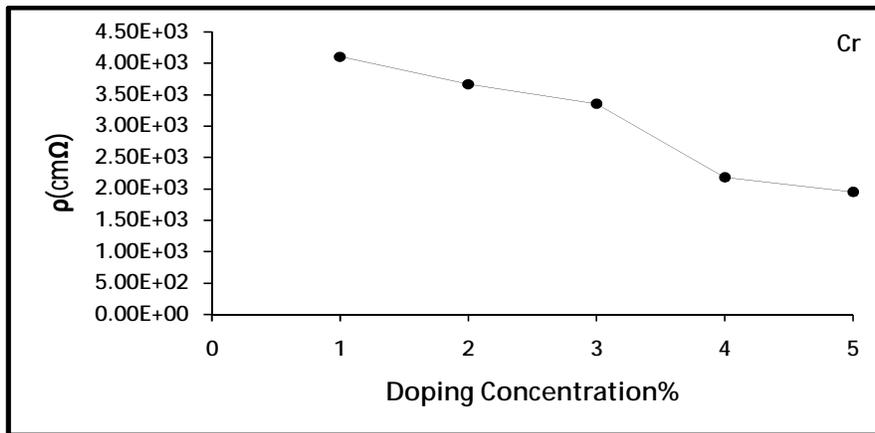


Figure (6): The electrical resistivity as a function of different doping concentration with chromium.

Hall Measurement

The results obtained from Hall effect for Cr doping TiO₂ 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 TiO₂ thin 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 TiO₂ 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 NH₃ gas by pure TiO₂ and doped TiO₂ were investigated as a function of time operation . These films have been grown on silicon (P-type) substrates by spray pyrolysis technique .The time dependence on sensitivity of different TiO₂ 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 TiO₂ and doped TiO₂ with chromium(Cr). Change in resistance are shown with time. The resistance of pure TiO₂ 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 TiO₂ films. A minimum resistance is of TiO₂ doped with (5%) chromium . The resistance decreases drastically during the gas exposure, a maximum resistance started to increase in TiO₂ pure.

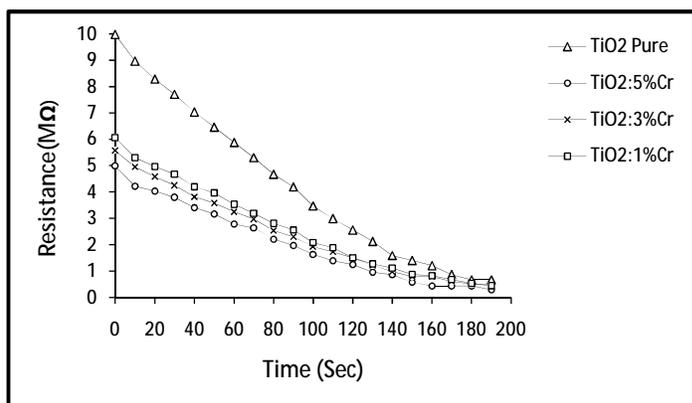


Figure (7) :Resistance of TiO₂ pure and doped with chromium as a function of operation time for NH₃ gas .

Operation Time Effect on Sensing Properties

The gas sensitivity of undoped and doped TiO₂ films is calculated from measuring the resistance change in thin films in air and in gas . Figure (8) shows the gas sensitivity of undoped TiO₂ 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 TiO₂ is less than sensitivity of doped TiO₂ because the surface species and trapped electrons are returned to the conduction band causing an increase in the conductivity of the TiO₂ films doped with respectively chromium and the sensitivity of the sensor increases.

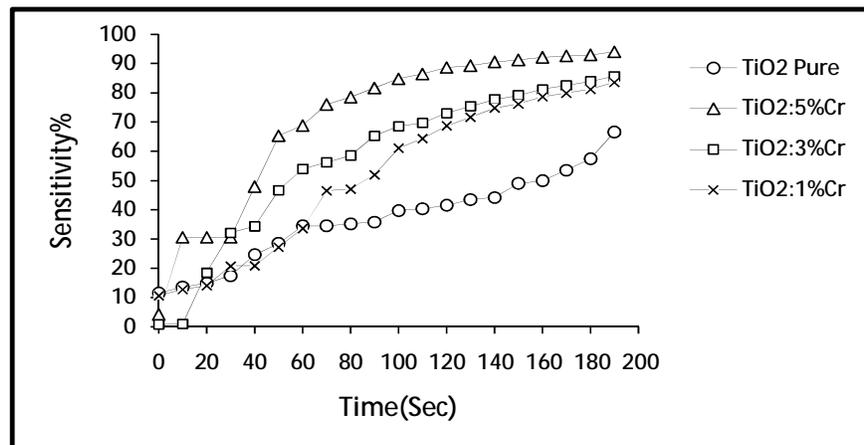


Figure (8) :Sensitivity of TiO₂ pure and doped with chromium, films for NH₃ gas at different operation times.

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 TiO₂ 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 TiO₂ films. Hall measurement indicate that the TiO₂ doping with Cr thin films have same conduction type (n-type) conductivity. The sensor TiO₂ doped with Cr shows good sensitivity to NH₃ gas.

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