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Optimization of Rutile/Anatase Ratio in Titanium Dioxide Nanostructures prepared by DC Magnetron Sputtering Technique

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Abstract

Mixed phase rutile/anatase of TiO_2 was prepared and studied by a closed field DC magnetron sputtering configuration (CFDCMS). It was found that the contents of rutile increased from the ratio of 38% to 53% as the deposition time increased from 3.5 hours to 4.5 hours.

The photocatalytic activity of the mixed phase rutile/anatase TiO_2 was measured by monitoring the degradation of the blue methylene dye in an aqueous solution, under exposure to UV-radiation, using UV-vis absorption spectroscopy. It was proven that the photocatalytic activity in the mixed phase (TiO_2) is a function of rutile content reaching a maximum value at 53% rutile. Thus, the effect of synergy between anatase- TiO_2 and rutile- TiO_2 was observed. It was observed that TiO_2 rutile is far less active than TiO_2 Anatase. Yet, the presence of the two phases together results in considerable enhancement of the reaction rate when compared to TiO_2 anatase alone. This may be due to the increase of the charge carriers' lifetime allowing for electrons transfer to hydrogen ions and holes transfer to oxygen ions.

Keywords: TiO_2, Thin Film, Mixed TiO_2 Phase, Photocatalysis, DC Magnetron Sputtering Technique.

تحديد النسبة المثلى لطوري الروتايل/أناتاس لتراكيب ثنائي أوكسيد التيتانيوم النانوية المحضرة بتقنية الترذيذ الماكنتروني المستمر

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الخلاصة

جرى تحضير تراكيب ثنائي أوكسيد التيتانيوم النانوية ذات الطور المختلط (روتايل/أناتاس) باستخدام تقنية الترذيذ الماكنتروني التفاعلي المستمر بتوظيف المجال المغلق (CFDCRMS) ومن ثم دراسة خصائصها التراكيبية وفعالية التحفيز الضوئي لها. وجد أن نسبة طور الروتايل في العينات النهائية قد ازداد من 38% إلى 53% مع زيادة زمن الترسيب من ثلاث ساعات ونصف إلى أربع ساعات. جرى قياس فعالية التحفيز الضوئي للعينات المحضرة ذات الطور المختلط من خلال مراقبة تحلل صبغة المثيلين الزرقاء في محلول مائي عند تعريضها للأشعة فوق البنفسجية. وقد تأكد لنا أن فعالية التحفيز الضوئي تكون دالة لنسبة الروتايل في عينة ثنائي أوكسيد التيتانيوم إذ تصل أقصى قيمة لها عندما تكون نسبة الروتايل 53% في العينة النهائية. من خلال ملاحظة تأثير التآزر ما بين طوري الروتايل والأناتاس فقد وجد أن طول الورتايل أقل فعالية بكثير من طور الأناتاس، وعليه، فإن وجود الورين معاً في عينة ثنائي أوكسيد التيتانيوم يؤدي إلى تحسن كبير

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في معدل التفاعل بالمقارنة مع العينة التي تكون بطور الأناتاس فقط. ويمكن أن يعزى ذلك إلى زيادة فترة حياة حاملات الشحن مما يسمح للإلكترونات بنقل إلى أيونات الهيدروجين فيما يسمح بنقل الفجوات إلى أيونات الأوكسجين.

1. Introduction

Titanium dioxide (TiO_2) films has been enormously investigated in recent years because of its potential applications in a wide range of fields such as solar cells, gas sensors, memory cell capacitors, as well as in photocatalysis applications like water treatment, self- cleaning effect, anti-fogging effect, air-cleaning effect and anti-bacterial coatings [1–3].

The photocatalytic activity of pure-TiO_2 is known to be dependent on the various material parameters, which include the average nanocrystallite size, powder morphology, specific surface area, crystallinity, and phases involved. [4, 5].

Out of the two popularity of phases of TiO_2, the mixed TiO_2 phase anatase/rutile, have higher photocatalytic activity than that of the single anatase or rutile phase, which is ascribed to synergistic effect between the two phases [6]. The co-presence of anatase and rutile crystallites induces the high level of photocatalytic activity; transfer of photo excited electrons and positive holes between interconnecting anatase and rutile particles (as shown in Figure-1) may enhance charge separation and hence improve the efficiency of utilization of electron-hole pairs [7]. Further characterizations affirmed the electron transfer between the two phases and suggested that phase composition is a fundamentally important factor in high photocatalytic activity [8].

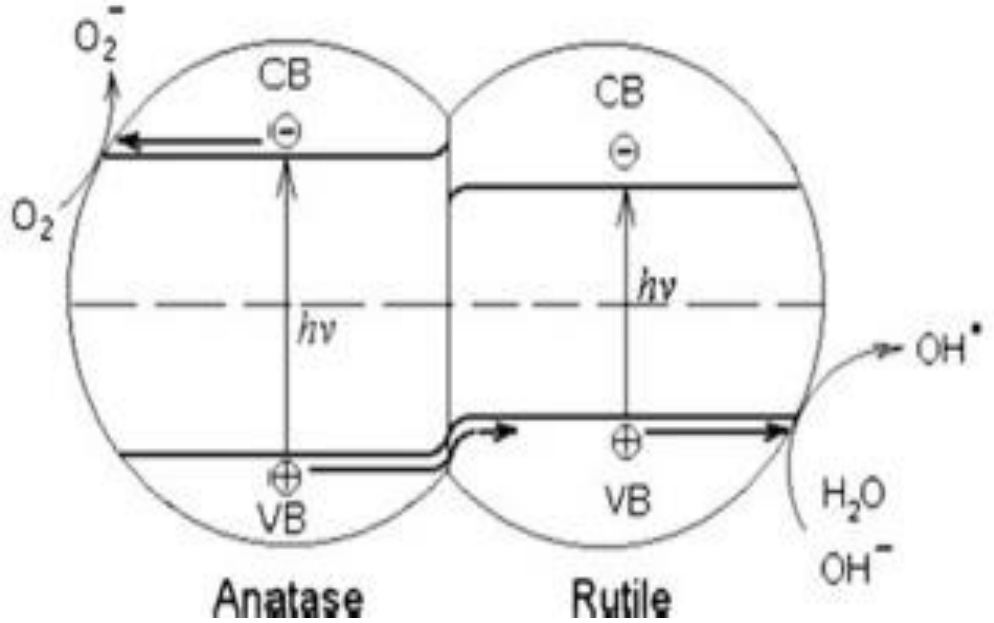

Figure 1-Mechanism for the synergistic effect of rutile and anatase mixed-phase [9]

The present work focuses on the study of the effect of some sputtering parameters in the optimization of rutile percentage quantity in mixed phase nanocrystalline TiO_2. This will predict the relation between the structural phase and photocatalytic activity of TiO_2.

2. Experimental details

Closed field DC reactive magnetron sputtering system (shown in Figure-2) was employed . The two electrodes (anode and cathode) are stainless steel disc of 8 cm diameter and 4 The electrodes were connected to a DC power source to provide the necessary electric power for the discharge (the discharge voltage 3 kV and discharge current of 50 mA). The lower electrode (anode) could be moved vertically with respect to the fixed upper electrode (cathode) to adjust the separation of the two electrodes to (4cm). A high purity (99.99%) Titanium sheet was connected to the upper electrode as a target. For the evacuation of the discharge chamber, two stage rotary pump (Edward 8 m^3/h) was operated to a base pressure of about 3×10^{-2} mbar.

At the beginning of film preparation, a glass substrate was exposed to pure argon gas to produce the discharge plasma, then argon (Ar) and oxygen (O_2) gases were used as sputtering and reactive gases, respectively. The flow ratios of Ar:O_2 were controlled by a gas flow controller unit (as shown in Figure-2) at gas mixture ratios (10:10) for different deposition time (3.5, 4 and 4.5 hour) without any heating to the sample. The flow gas mixture was interred into the chamber while pressure was kept constant (7×10^{-2} mbar). There was no intentional substrate heating in this work.

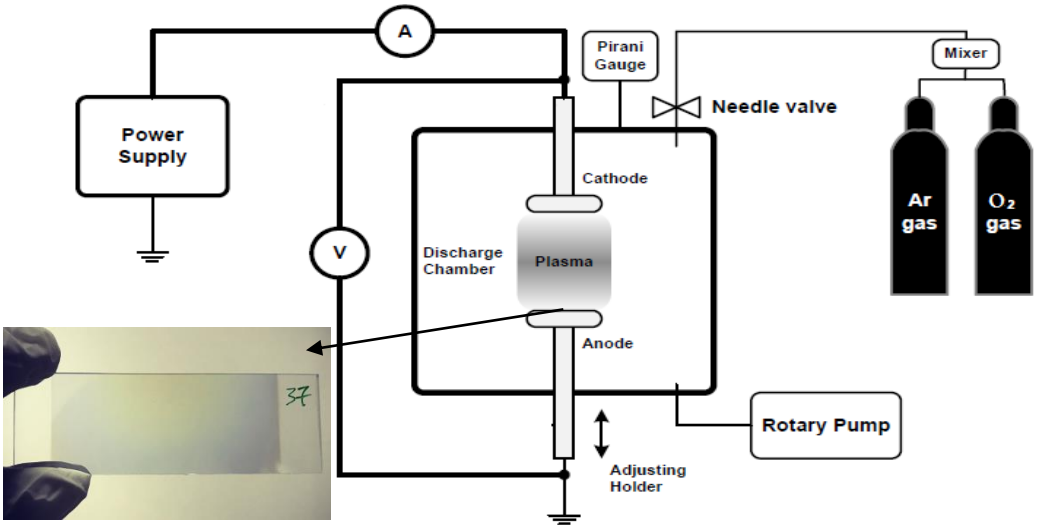

Figure 2-Schematic diagram of the home made CFDCMS configuration

The Photocatalytic Activity test of the TiO_2 mixed phase monitoring degradation of methylene blue dye (MB) in aqueous suspension containing TiO_2 nanoparticles was done under UV-radiation exposure. 50 ml of aqueous suspension was prepared by dissolving 0.0159 g of MB dye in deionized water. The MB dye was placed in putter dish with nanocrystalline TiO_2 thin film with stirring in the dark (without the UV-radiation exposure) for 1 h to stabilize the adsorption of the MB dye over the surface of TiO_2 nanoparticles.

3 mole of the aqueous suspension was exposed toUV radiation (200-400nm) in the ultraviolet unit

3. Results and Discussion

The crystalline structure of the prepared samples at different sputtering parameters were investigated by XRD as shown in Figure-3.

The TiO_2 phase structures are shown in the diffraction pattern peaks at 2θ values of (25°, 36°, 37°, 47°, 53°, 55°, 62°, 70° and 75°).This confirms the existence of the TiO_2 anatase structure and agrees with the JCPDS card no. 21-1272 (anatase TiO_2) [10]. While the peaks at (27°, 40° and 56°) correspond to the rutile phase in TiO_2 and agrees with the JCPDS card no. 00-021-1276 (rutile TiO_2) [11].

The weight fraction of the rutile phase in an anatase-rutile mixture can be determine by the relation [12]:

$$f = \frac{1}{1+1.26\frac{I_R}{I_A}} \quad \text{..... (1)}$$

Where f is the weight fraction of rutile in mixed phase anatase/ rutile and (I_R/I_A) is the ratio of the intensity of the rutile to the intensity of the anatase that is determined from the x-ray intensities. It is clear that the increase in the deposition time introduces an improvement in the crystallinity of the deposited films with the formation of a rutile phase. The relative amounts of rutile in mixed phase anatase/rutile increased from 38% to 43% and 53% rutile with the increase of the deposition time from 3.5 h , 4 h and 4.5 h, respectively.

FTIR spectra, in the range 400 to 4000 cm^{-1}, were recorded using the spectrometer FTIR (supplied by Shimadzu-8400S) for the prepared samples as shown in Figure-4. The structure al of TiO_2 was clearly observed in these spectra for all the prepared samples. The band assigned to Ti-O stretching vibration was observed at around 447 and 667cm^{-1} while the peak at 408.91 cm^{-1} is due Ti-O-Ti

bonds in the TiO_2 lattice. The peaks at around 3450 and 1620 cm^{-1} are due to the stretching and bending vibration of the OH group in water molecules in atmosphere [13, 14]. The FTIR shows the absence of any impurities inside the prepared samples this is because of the optimum operating conditions used in the sputtering system.

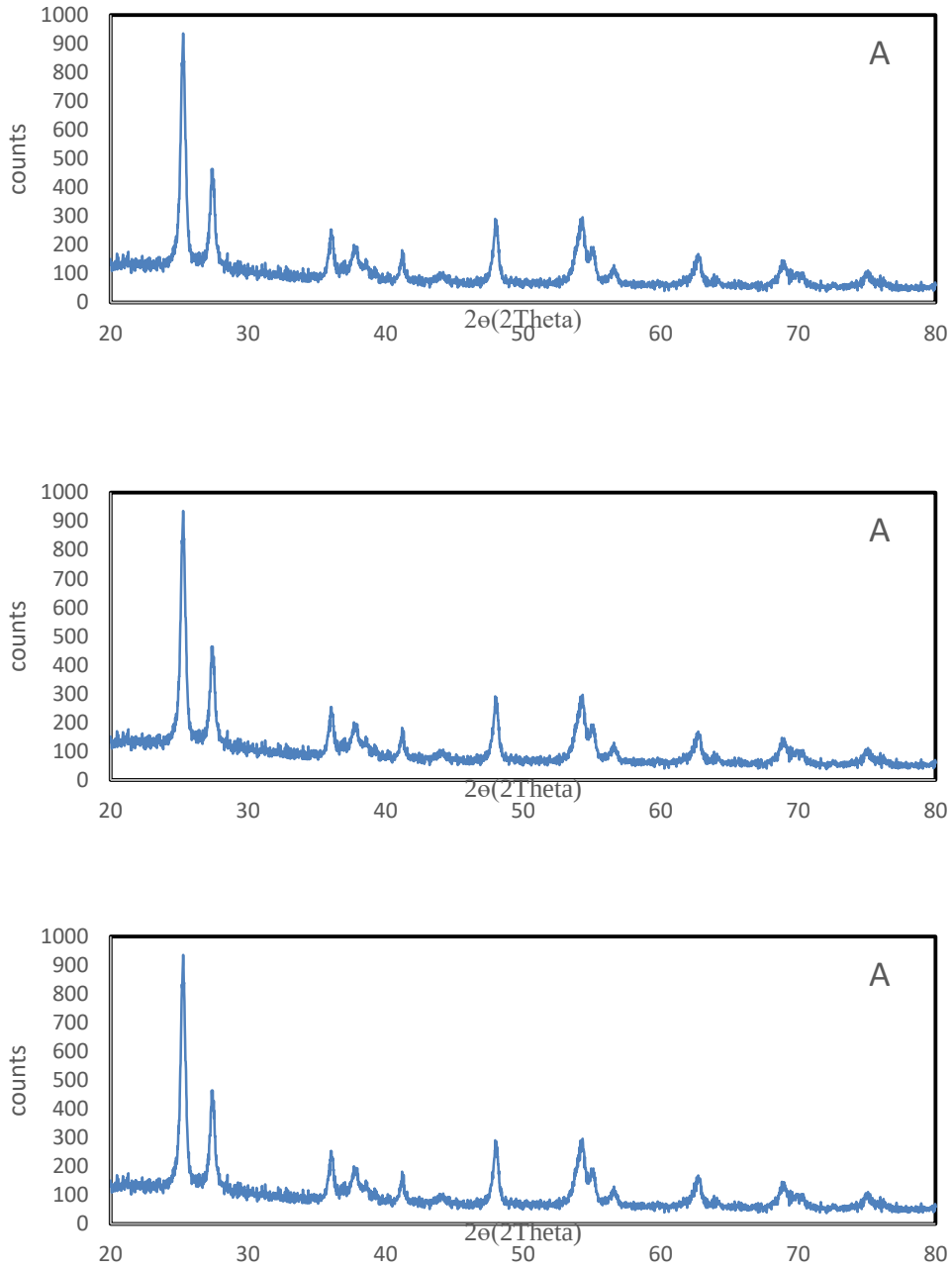

Figure 3-Broad-scan XRD spectra obtained for mixed-phase nanocrystalline TiO_2 processed via D.C. CFRMSS at deposition time (a) 3.5 hour, (b) 4 hour, and (c) 4.5 hour .A and R represent diffraction peaks corresponding to anatase-TiO_2 and rutile-TiO_2, respectively.

Surface morphology and grain size for the optimized thin films are observed in the images of the scanning electron microscope. Figure-5 shows the SEM images for the mixed phase anatase/rutile TiO_2 sample with 43% rutile. The scale of these images are 200nm and 100nm. The grain size of TiO_2 nanoparticles that was recorded from these image is round (15) nm. The images clarify that the surface of this film was homogenous nanostructured and the particles were uniformly distributed with no

cracks. The energy dispersive X- ray (EDX) spectrum was recorded and analysed as seen in Figure- 6. The existence of Ti and O of weight ratio of Ti: O was found to be 24.6: 75.4. The EDX spectrum also shows that the structure of TiO_2 was homogeneous with high purity which matches the FTIR result.

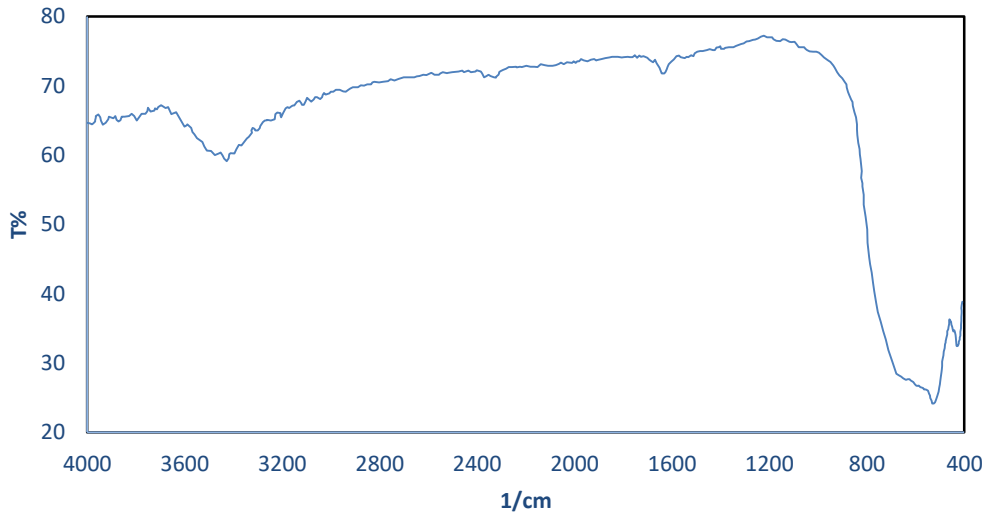

Figure 4-FT-IR spectra of TiO_2 sample with relative amounts of rutile of 43%.

UV-vis absorption spectra of mixed-phase nanocrystalline TiO_2, containing different amounts of rutile, are shown in Figure-7. A red shift in the absorbance spectra is observed as rutile content increases. Significant increase in absorption of wavelengths from less than 370 nm to 385 nm and over 400 nm, with increased rutile intake from 38% to 43% by weight and 53% by weight respectively was observed

To calculate the energy band gap of mixed-phase nanocrystalline TiO_2, absorption spectra of the prepared samples were measured using the spectrophotometer for the wavelength range 166-962 nm. The energy band gap was determined by the following equation [15]:

$$\alpha = A\,(h\nu - Eg)^n / h\nu \qquad \text{.....(2)}$$

where α is the absorption coefficient, Eg is the optical energy band gap, A is constant, h is Planks constant, ν the frequency of light, n is a given value that depends on the nature of the optical transition. The value of n=0.5 is assigned when the indirect allowed transitions are the dominant. From The intercept of linear behavior of $(\alpha h\nu)^{1/2}$ versus $h\nu$ – in Figure-8 – the band gap of mixed-phase nanocrystalline TiO_2 with amount of rutile 38 wt% was calculated to be 3.37eV. With increasing the amount of rutile to 43 wt% the band gap becomes 3.22 eV. For mixed-phase nanocrystalline TiO_2 with 53 wt% rutile is distinctly noticeable with the calculated band-gap value of 3.12 eV.

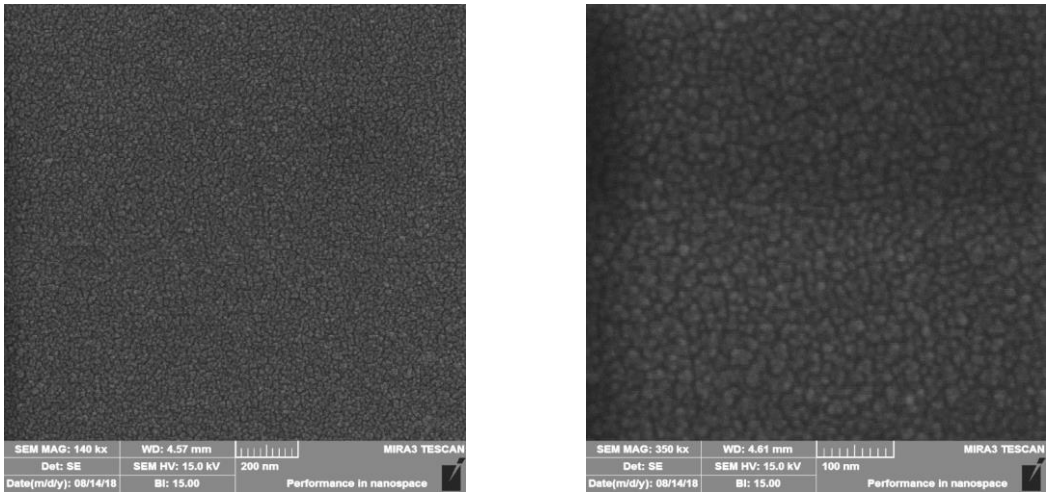

Figure 5-SEM image of TiO_2 sample with relative amounts of rutile of 43%.

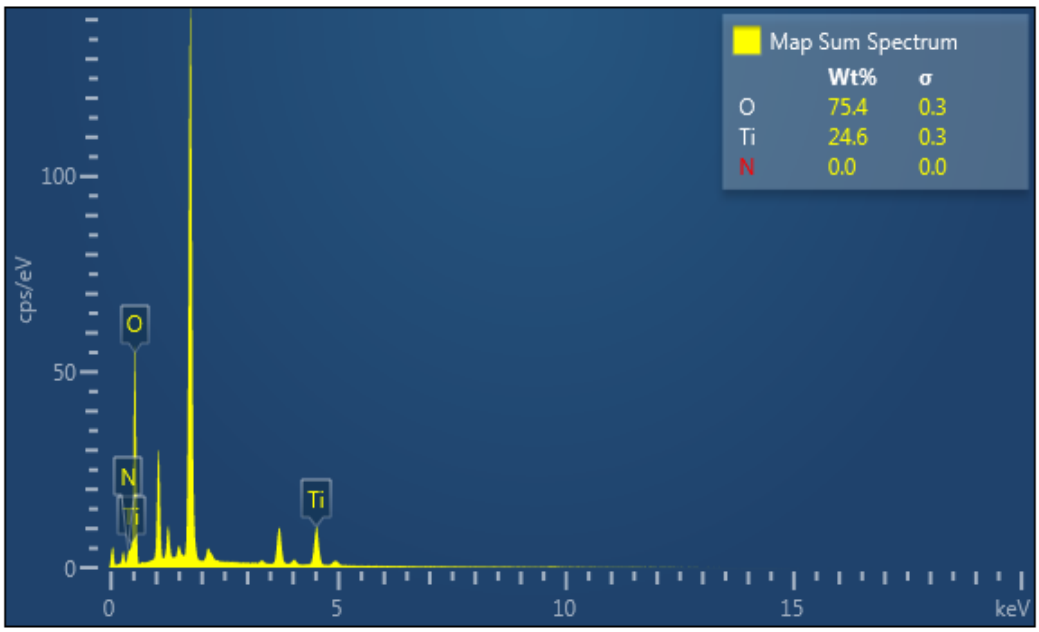

Figure 6-EDX image of TiO_2 sample with relative amounts of rutile of 43%.

Photocatalytic Activity of Mixed-Phase Nanocrystalline TiO_2 processed by the DC Magnetron Sputtering technique through observing the decomposition of dye methylene blue (MB) in an aqueous suspension system that has a thin film nanocrystalline of TiO_2 under exposure to UV radiation was studied with a spectrophotometer to study the degradation of the MB dye.

Absorption spectra of the dye solution of MB as a function of the time of exposure to UV-radiation were recorded. The maximum absorption peak (A) of the MB dye solution at 656 nm was taken at concentration (C). The UV-vis absorption spectra of MB dye solution, without addition of TiO_2 nanocrystalline and exposure to UV-radiation, was taken as a reference spectrum corresponding to the concentration of the initial dye MB (C_0).

The normalized residual MB dye concentration after dye degradation was calculated using the following equation [16]:

$$\left(\frac{C}{C_O}\right)_{MB} = \left(\frac{A_{time=t}}{A_{time=0}}\right)_{656\,nm} \quad \ldots\ldots\ldots\ldots (3)$$

This equation shows the kinetic of the activity photocatalytic calculated in border of the degradation of the MB dye. So that, after the process, TiO_2 with rutile content of 53 wt% show more dye degradation than that at 38 wt% and 43 wt%, with the MB dye (as shown in Figure-9 (a).The addition of rutile to anatase TiO_2 introduces strong electronic interaction between them, due to improve in the kinetics of the photocatalytic activity of the mixed-phase nanocrystalline TiO_2.

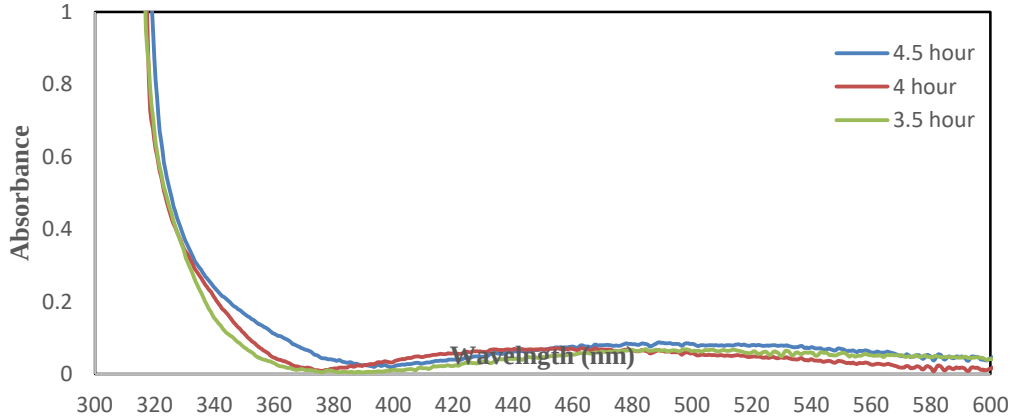

Figure 7-Absorption spectra for the prepared samples of TiO_2 at deposition time 3.5 hour (rutile content 38 wt.%), 4 hours (rutile content 43 wt.%) and 4.5 hours (rutile content 53 wt.%)

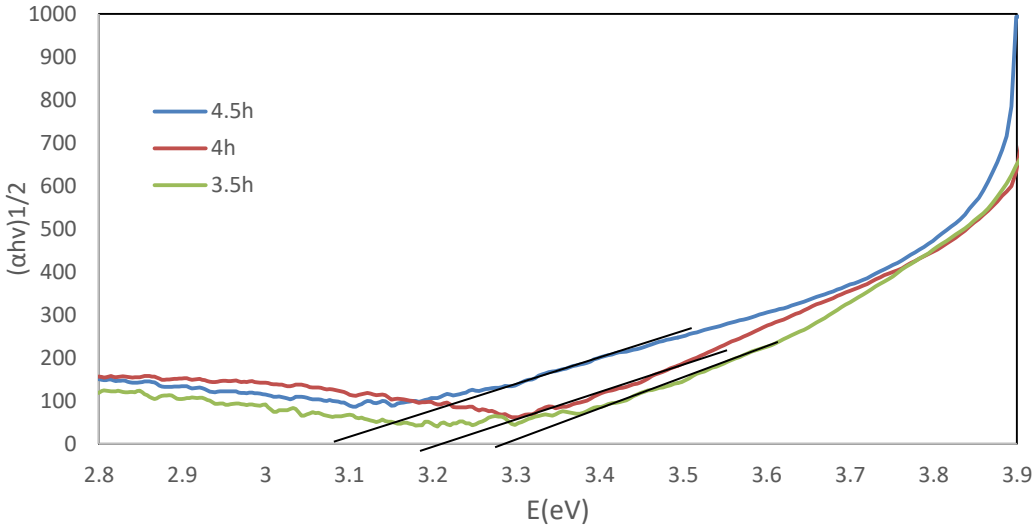

Figure 8-Energy band gap determination of TiO_2 samples at deposition time 3.5 hour (rutile content 38 wt.%), 4 hours (rutile content 43 wt.%) and 4.5 hours (rutile content 53 wt.%).

A photocatalysis experiment was also implemented in the absence of nanocrystalline TiO_2 photocatalyst to prove the constancy of the MB dye with continuous UV-radiation exposure. Under this condition, the initial MB dye concentration (C_0) stay unchanged even after irradiating the sample for a total time of 210 min. as shown in Figure-9(b).

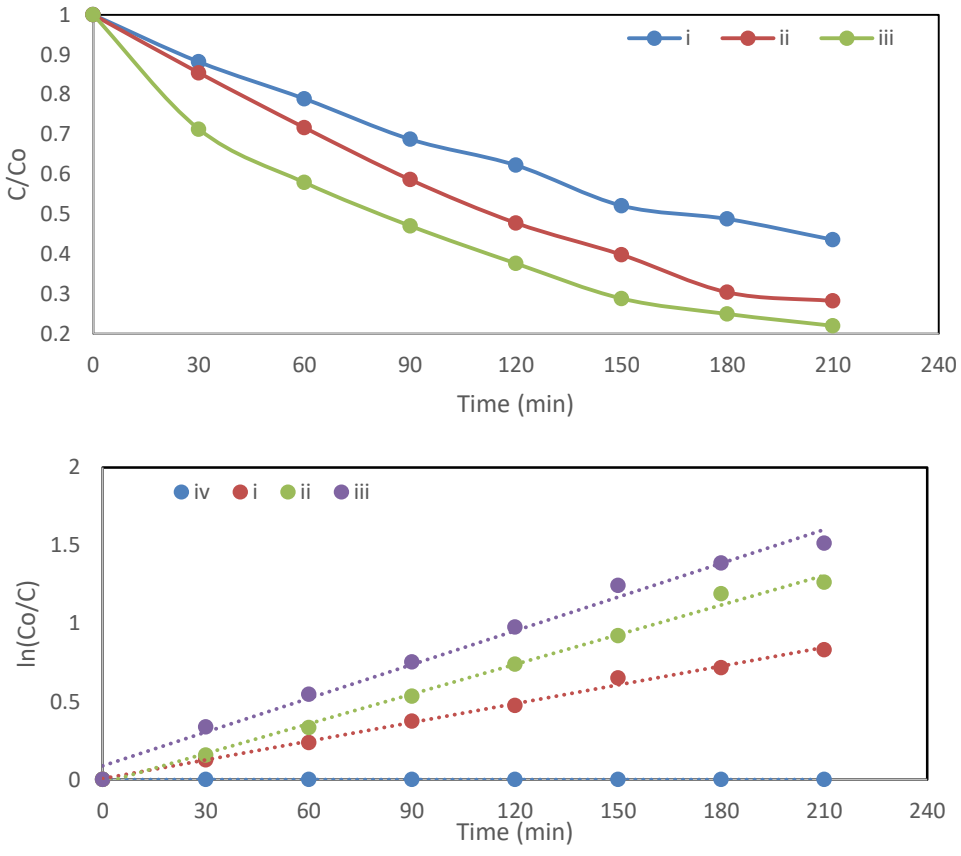

Figure 9- (**a)** Typical variation in the normalized residual MB dye concentration as a function of UV-exposure time, obtained for the mixed-phase nanocrystalline TiO_2 processed via DC Magnetron Sputtering Technique with a rutile content of (i) 38 wt.%,(ii) 43 wt.%,, and (iii) 53 wt.%, (iv) absence of nanocrystalline TiO_2 **(b)** Typical plots, obtained using part a

4. Conclusions

TiO_2 films with tunable phase structure were fabricated using direct-current reactive magnetron sputtering technique without any thermal treatment. The relative amounts of rutile in an anatase-rutile mixture was about 38%, 43%, and 53% rutile with the increase of deposition time to 3h ,3.5h and 4 h, respectively. The mixed-phase nanocrystalline TiO_2 with 53 wt% rutile showed shift in the absorbance peak above 400 nm with a calculated value of band-gap of 3.12 eV.

it was also observed that the photocatalytic activity of the nanocrystalline TiO_2 was variable with the rutile content . Where TiO_2 with rutile content of 53 wt% showed the highest degradation of the MB dye

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