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Study the structural and optical properties of titanium oxide thin film, doped with chromium prepared in Sol-Gel method

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Abstract

This paper presents the effect of Cr doping on the optical and structural properties of TiO_2 films synthesized by sol-gel and deposited by the dip- coating technique. The characteristics of pure and Cr-doped TiO_2 were studied by absorption and X-ray diffraction measurement. The spectrum of UV absorption of TiO_2 chromium concentrations indicates a red shift; therefore, the energy gap decreases with increased doping. The minimum value of energy gap (2.5 eV) is found at concentration of 4 %. XRD measurements show that the anatase phase is shown for all thin films. Surface morphology measurement by atomic force microscope (AFM) showed that the roughness of thin films decrease with doping and has a minimum value with 4 wt % doping ratio.

Key words
TiO_2 doping, sol-gel, dip-coating.

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دراسة الخصائص التركيبية والبصرية لأوكسيد التيتانيوم، المطعم بالكروم والمحضر بطريقة سول-جل

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الخلاصة

يعرض هذا البحث تأثير التطعيم بالكروم على الخواص البصرية والتركيبية لأغشية TiO_2 المحضرة بواسطة طريقة السول-جل والمرسبة بواسطة تقنية الطلاء بالغمر. وقد تم دراسة خصائص كل من TiO_2 النقي و المطعم بالكروم بواسطة قياسات الامتصاص و حيود الأشعة السينية (XRD). يشير نطاق الامتصاص للعديد من تركيزات الكروم TiO_2 إلى ازاحة باتجاه المنطقة الحمراء؛ وبالتالي، فإن فجوة الطاقة تقل مع زيادة التركيز. ان القيمة الدنيا لفجوة الطاقة (2.5eV) وجدت عند التركيز 4 ٪. تبين قياسات XRD أن طور الانتس anatase يظهر في كل الأغشية الرقيقة. تمت دراسة طبيعة السطح للعينات باستخدام مجهر القوة الذرية (AFM). اظهرت الفحوصات باستخدام مجهر القوة الذرية ان خشونة السطح تقل عند التطعيم ولجميع النسب وان اقل خشونة للسطح ظهرت عند نسبة التطعيم 4 %.

Introduction

Titanium dioxide (TiO_2) has been reported widely recently for its visually interesting characteristics, electronic properties and good stability in natural environments, for high refractive index, wide band gap and chemical stability, polycrystalline TiO_2 films for a variety of uses such as optics fabrications [1], dielectric usages [2], dye sensitized solar cell (DSSC) [3], self-cleaning [4], and photocatalytic applications [5].There are many ways to prepare TiO_2 and there thin films [6, 7]. The photo-catalytic properties of TiO_2 was first determined by Fujishima and Honda in 1972 [8]. TiO_2 can be found as an amorphous layer and also in three crystalline phases: brookite (orthorombic), anatase (tetragonal), and Rutile (tetragonal). Only the rutile phase is stable thermal dynamics at high temperature. The refractive index at 500 nm relative to the bulk anatase and rutile titanium dioxide are about 2.5 and 2.7 respectively [9]. There are many deposition approaches for preparing TiO_2 thin films, such as electron beam evaporation [10], DC magnetron sputtering [5], Sol-gel technique [7], RF reactive magnetron sputtering [3], and plasma enhanced chemical vapor deposition [2]. In this work, Dip-coating method was used to prepare thin films with drawing speed 9 mm/s. The films were deposited on normal microscope slides substrates. Optical, morphological and structural profiles were performed by UV-Vis spectrometer, AFM and XRD techniques.

Experimental part

Pure and TiO_2:Cr preparing

(TiO_2) sol was prepared using the following steps: Deionized water was mixed with Titanium tetra isopropoxide or (TTIP) in terms of a molar ratio of Ti: H_2O=1:100. To adjust the pH Nitric acid was used and for determining the hydrolysis process of the solution. The solution was set on a magnetic stirrer for (24 hours). The output product (transparent sol) was aged for 6 hours at 55 $^{\circ}$C. The dopant weight percentage of chromium was (2%, 4%, 6% and 8%) [11].

Thin film preparing

Get multi layers of coating (TiO_2) by immersing pre-cleaned substrates in solution (TiO_2) by dipping method using a dip-coater device. To avoid the sol perturbation, the substrates were stayed in the sol for one minute. After that, it was withdrawn with a fixed withdrawing speed of (9 mm/sec). The substrate was dried in an oven for (15 minutes) at (110 $^{\circ}$C). Finally, the calcination was done in a furnace for three hours, at (450 $^{\circ}$C) with a temperature rate of (20 $^{\circ}$C/min.).

Results and conclusion

UV-VIS absorption

Optical characterization was achieved by absorption spectra, where the band gap energies were calculated for the prepared samples. Fig.1 shows the absorption of TiO_2 doped by metal, in the spectral range (200-800) nm. It is clear that the absorption edge is moving toward red shift as relation to the naked sample in the direction of Cr-doped TiO_2.

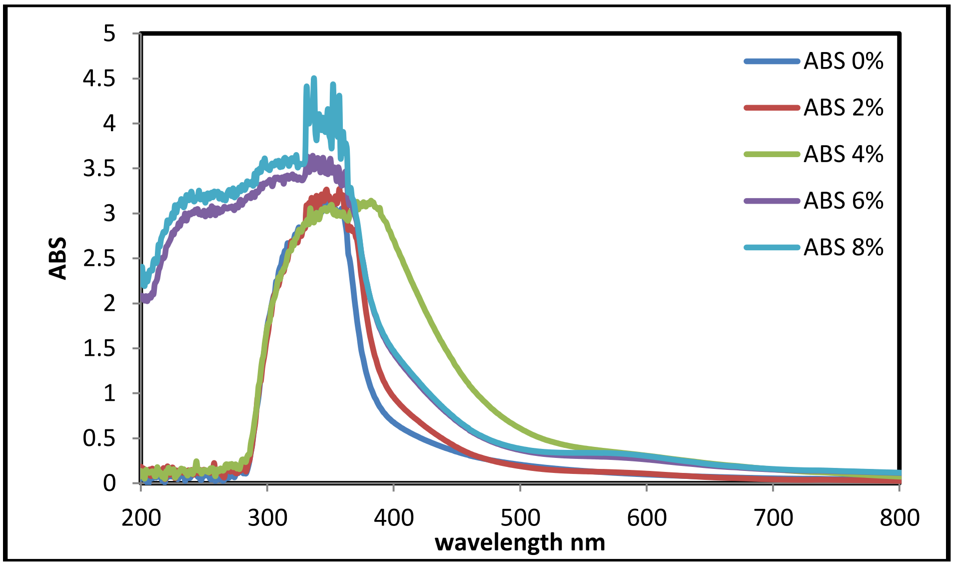

Fig. 1: Absorption of pure and Cr-doped TiO_2 samples.

Band gap energy

Fig.2 shows the calculate energy gap value for doped and undoped TiO_2 thin films, the energy gap was decreased for all doped thin films and take the least value with sample that doped with 4% wt.

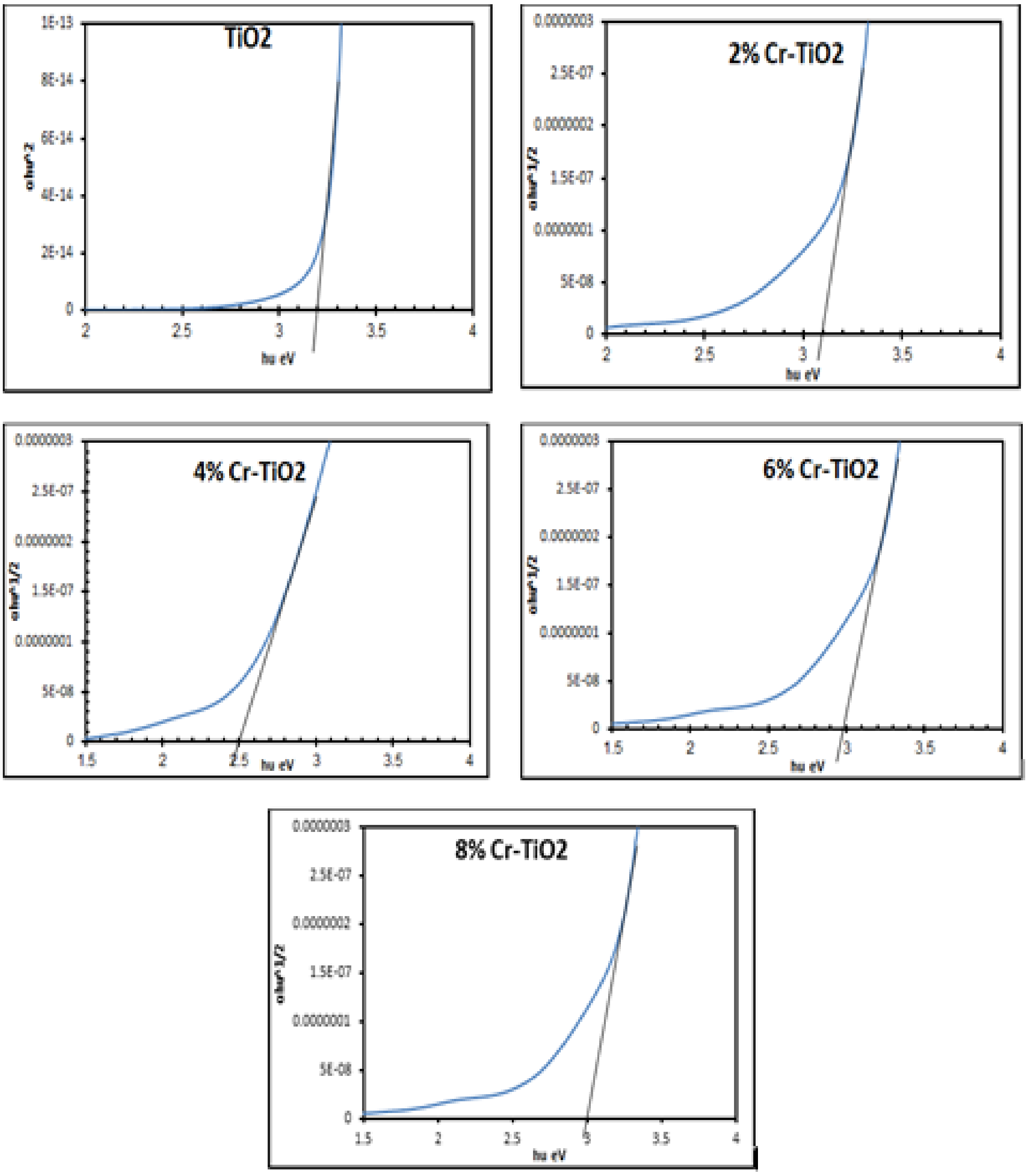

Fig.2: Band energy gap for all samples.

XRD analysis

X-ray pattern for samples are shown in Fig. 3. This fig shows that, the film was polycrystalline having totally anatase phase. It is observed that the films exhibited characteristic peaks of anatase crystal plane (101), (004), (200), (105) and (211). The nearly sharp peak detected at (25.14°) can be related to anatase phase with crystal plane (101), while the intensity of the other peaks is very weak.Crystalline size are illustrated in Table 1.

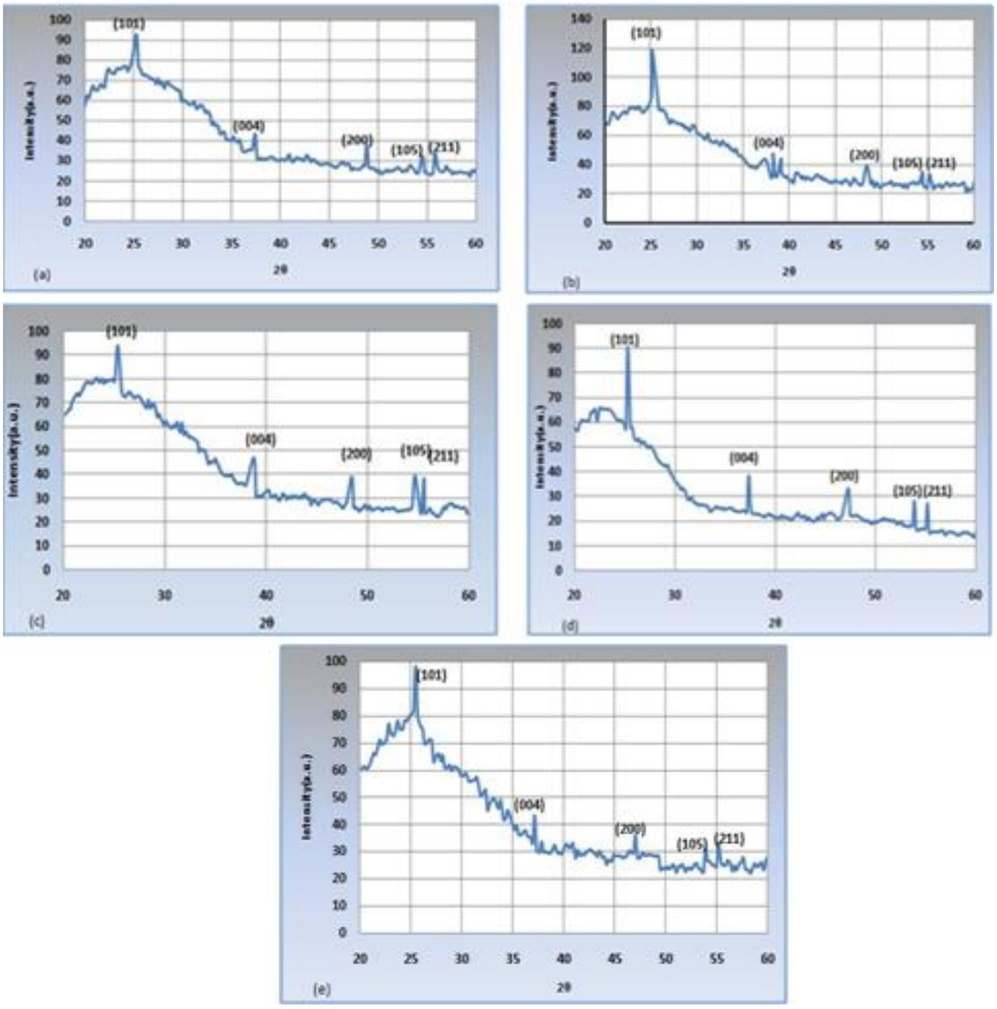

Fig.3: XRD for pure and Cr-doped TiO_2.

Table 1: Experimental X-ray peaks for (Cr- doped TiO_2) samples.

W%	2θ(degree)	FWHM(degree)	Crystalline size (nm)	hkl	Phase
2%	25.36	0.47	32.6	(101)	Anatase
4%	25.19	0.74	20.8	(101)	Anatase
6%	25.27	0.44	34.8	(101)	Anatase
8%	25.5	0.41	37.5	(101)	Anatase

Through Table 1 it is clear that the least crystalline size will be at the concentration 4 % and this is consistent with XRD measurement.

AFM measurements

In order to calculate the surface roughness and morphologies of the samples belong to pure and Cr doped TiO_2, atomic force microscopy (AFM) technique has been used. The atomic forces microscopy images (2588 × 2562.87 nm^2) of the films prepared on glass substrate at 450°C under air atmosphere are shown in Figs. 4-8.

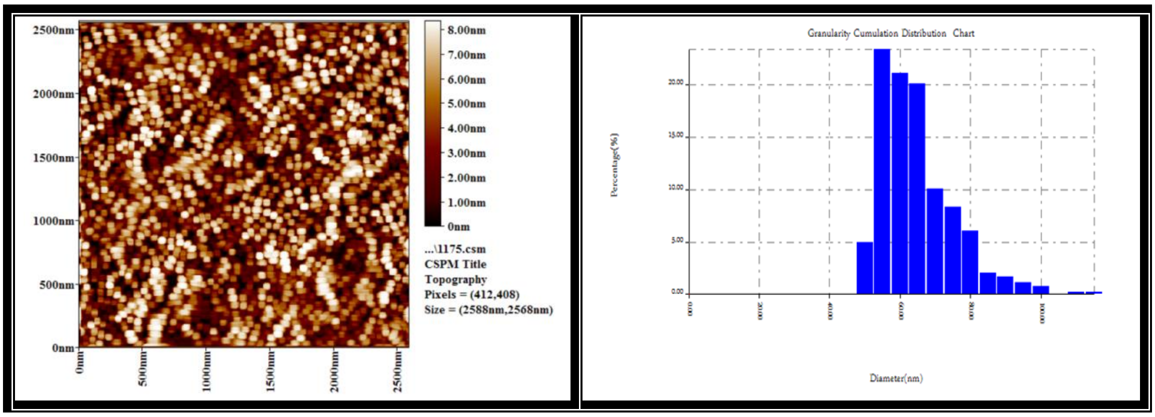

Fig.4: Surface roughness and histogram of pure TiO_2 sample.

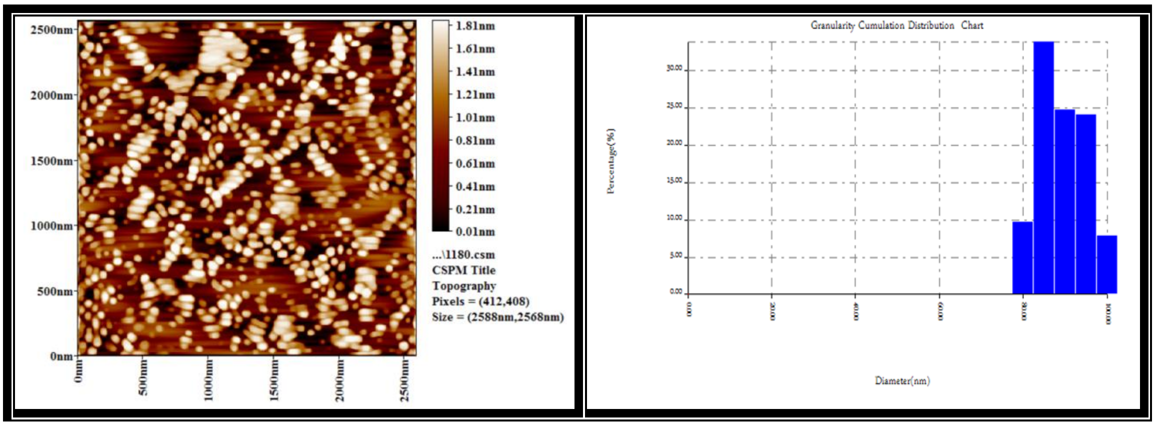

Fig.5: Surface roughness and histogram of Cr-doped TiO_2 (2%) sample.

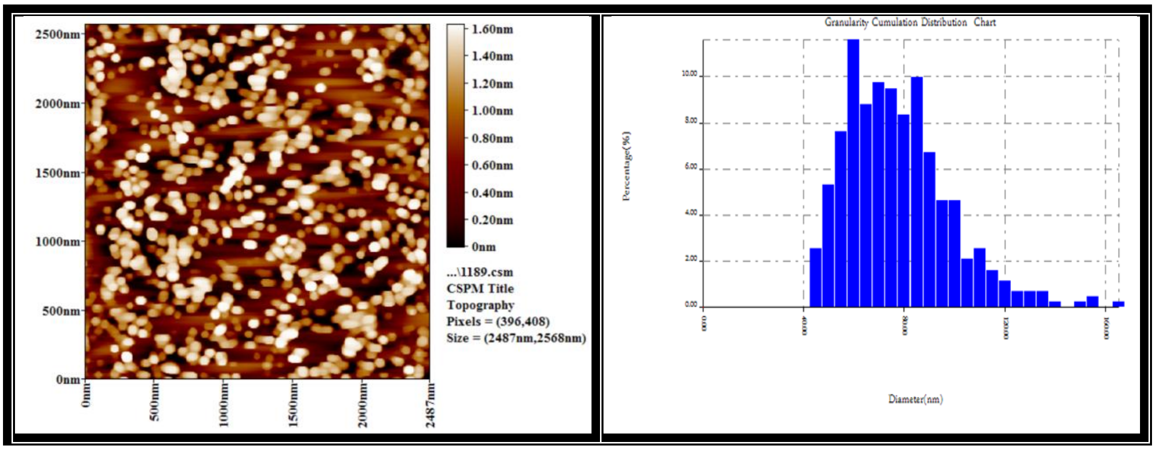

Fig. 6: Surface roughness and histogram of Cr-doped TiO_2 (4%) sample.

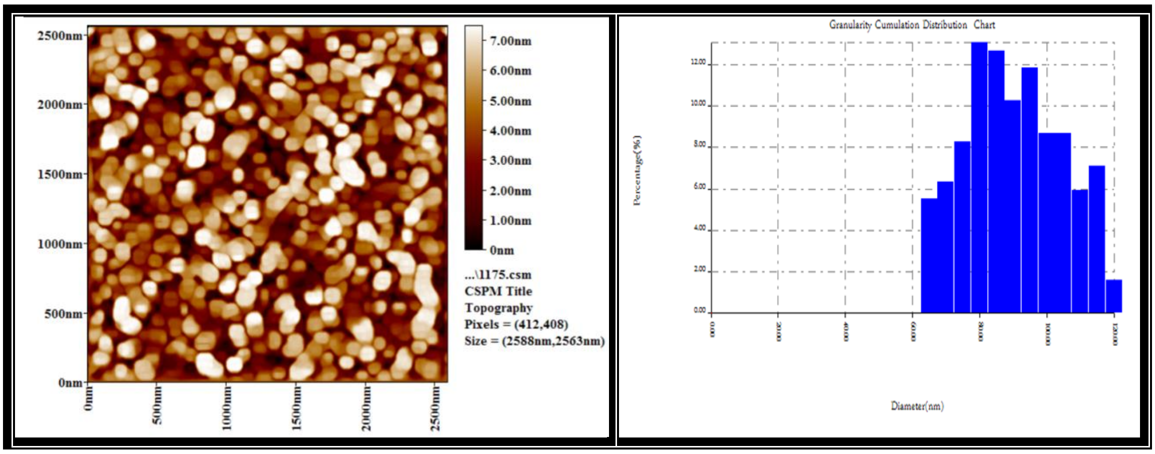

Fig.7: Surface roughness and histogram of Cr-doped TiO_2 (6%) sample.

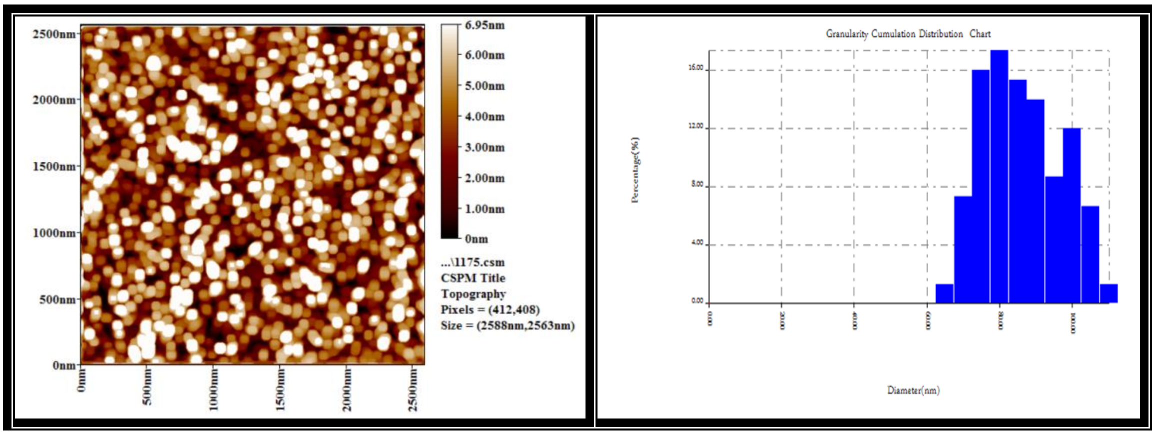

Fig.8: Surface roughness and histogram of Cr-doped TiO_2 (8%) sample.

nanoparticles can be densely packed in the films with properly uniform surface. Table 2 illustrates the mean average roughness of the surface and root means square roughness Rms, of these films. The surface roughness of films is very small for the films that doped by chrome where, the (Rms) roughness was in range of 0.476 – 1.94 nm. The quite lower at 4% concentration.

Table 2: AFM measurements.

W%	Roughness Rms (nm)	Roughness average (nm)	Height (nm)	Surface area ratio
0	2.410	2.090	8.34	2.0200
2	0.532	0.461	1.84	0.0731
4	0.476	0.414	1.63	0.0571
6	1.960	1.660	4.17	0.4950
8	1.940	1.640	4.15	0.8750

The nucleation sites are likely to increase at the case of glass substrates and the atoms have relatively high energy, which results in a decrease in the grain size and the roughness and increase in the uniformity of the surface as mentioned above in the figures. This result agree with Mardare et al. (2000) [12].

Conclusion

Pure TiO_2 and Cr- doped TiO_2 nanoparticles were successfully synthesized via Sol-gel technique using

Titanium tetraisopropoxide (TTIP) as a precursor. Cr- doped TiO_2 samples were prepared, using $Cr(NO_3)_3$ as the dopant sources of Cr . The amount of dopants were varied in four concentrations, 2, 4,6 and 8 mol%. The obtained products were characterized by several techniques, such as UV-VIS spectroscopy, energy gap , XRD,AFM techniques. By using Sol-gel technique totally anatase phase can be exhibited in the thin film that's confirmed by XRD measurements. the band gap energies decreased from 3.2 eV (undoped TiO_2) to 2.5 eV for 4% of Cr-doped TiO_2 .This corresponds to the shift of absorption spectrum from near UV into visible region. The results presented by AFM illustrate that the TiO_2 thin film surface roughness was decreased after Cr doping.

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