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DEPOSITION OF TiO_2/PT COMPOSITE PARTICLES USING PULSED LASER DEPOSITION TECHNIQUE

Amin Daway Thamir [1], Adawiya J. Haider [2], Ghalib A. Ali [3]
[1, 2] Professor, [3] Assistant Lecturer
[1, 3] Production and Metallurgy Engineering Department, University of Technology
[2] Center of Nanotechnology, University of Technology
E-mail: ghalibalzobaidy@yahoo.com, prof.adawiya@ uotechnology.edu.iq
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ABSTRACT:- In the present work, the titanium oxide platinum (TiO_2/Pt) composite particles were deposited on the Si and glass substrates at (400)°C using pulsed laser deposition technique to ablation of TiO_2 target at constant laser energy 800 mJ, a double frequency Q-switching Nd: YAG laser beam (λ= 532 nm, repetition rate 6Hz and the pulsed duration 10ns). Ultraviolet visible (UV-Vis) spectroscopy, X-ray diffraction (XRD),X-ray fluorescence (XRF), Atomic force microscopy (AFM),Scanning Electron Microscopy (SEM), electrical conductivity (σ_{dc}), Hall coefficient (R_H) ,(I-V) and (C-V) were used to characterize the morphology and electrical of the films. The results showed that the transparency of film reached to about (80%) with optical band gap (3.64) and (3.76) eV for Pure TiO_2 and 5% Pt:TiO_2 respectively. The structural and composition of the obtained films at level 5% of platinum doping into TiO_2 have been determined. The results indicated that the prepared films (Pt doped TiO_2) were nanostructure and uniform with diameters less than 20 nm.

Key words: Pulsed Laser Deposition Technique, Pt doped TiO_2

1- INTRODUCTION

Crystalline oxide films are important components in a wide array of electronic and optical devices, and their study also manufacture involve major aspects of current science and technology. NanocrystallineTiO_2 is a multifunctional material that has many important applications including photocatalaysis and antireflection coatings (1, 2). The large band gaps make titanium oxide (TiO_2) a suitable material for important applications in photovoltaic devices including solar cells (3), mainly with anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal) crystalline structures; among this rutile is the most stable phase. The actual efficiency of TiO_2 depends not only on its phase composition, but also on its microstructure, particle size, morphology and porosity, which in turn is controlled by the synthesis method employed. Rutile-TiO_2 is known as white pigment because of its high scattering effect which leads to protection from the ultraviolet light (1, 4, 5). Pulsed laser deposition (PLD) is a versatile technique (6, 7). This method is used mainly because of the stoichiometric transfer between the target and deposition film and thus good controllability of the film composition (8). In the present paper, preparation of nanostructure TiO_2 thin films using laser ablation on heated glass substrates kept in vacuum is studied. Pulsed laser deposition (PLD) is a simple, low cost method to grow oxide films. Effects of film deposition conditions on the structural and optical properties of the films have been discussed.

2- . EXPERIMENTAL WORK

The TiO_2 / Pt thin films were deposited on cleaned glass and Si substrates by using pulsed Nd:YAG laser deposition technique at pulse duration 10 ns and λ= 532 nm were focused through 12cm focal length of converging lens on to a high purity titanium target (99.999% provided from Fluka com.) at 45° angle of incidence and doping concentration (5%) for noble metal (Pt) this growth concentration was optimum. The target rotated with frequency of 6 Hz. The pulse laser energy at the target surface was maintained at(400) ◦C and (800) mJ. The morphology of the films was studied using structure and optical microscope. The transmittance of the films was investigated in spectral range (300–1100) nm using UV-VIS (SP8001) Shimatzu double beam spectrophotometer. The crystal structure of the grown films was analyzed with XRD and XRF system Shimatzu (6000) using CuKα radiation. The Atomic Force Microscope AFM of this films was studied using Shimatzu AA3000 Scanning probe Microscope.

3- RESULTS AND DISCUSSION

The optical transmittance of TiO_2 films on glass that prepared by PLD was measured by UV-Vis spectrophotometer. Fig. (1) as shown the preparation at constant temperature substrate for the optical transmission in the range from (300-1100) nm at constant temperature (400) ºC and laser energy 800 mJ . It is also found that the average TiO_2 film transmittance goes beyond 80% in the near-infrared zone. This shows that one can use TiO_2 film as a window material in solar cells.

The optical absorption peaks as shown in Fig. (2) locating at (0.672,0.86,0.863,0.932) nm corresponding to the (700,800,900 and 1000 respectively). Further observation shows that the absorbance of the TiO_2 films increases although constant substrate temperature. This is probably ascribed to the increase in particle size and surface roughness. The other is that the part phase transformed from anatase to rutile leading to the decrease in the band gap.

The optical band gap films calculated depending on value of the transmittance for various wavelengths. The plots of $(\alpha h\upsilon)^2$ against hυ for films are shown in Fig.(3)The calculated band gap energies are (3.64 and 3.76) eV corresponding to the (400 ◦C pure TiO_2) and (5% pt: TiO_2)respectively, are lower than the bulk TiO_2, because of reduction in particle sizes reason due to the quantum confinement effect and increase of surface/volume ratio. The incorporation of dopant into TiO_2 lattice can cause a slight lattice disruption. Figures (3-a) and (3-b) show that the direct optical band gap decreases to give a shift. This shift is due to the increase in carrier concentration which results in filling that prevents the transition of the photo generate carriers into the filled levels according to quantum rules and hence leads so far to transition with larger photo energy. The band gap values are related to the crystallinity of the thin film. This decrease in energy gap can be due to the prohibited impurities that led to the formation of donor levels within the energy gap near the conduction band. Thus, it will absorb photons of low energy. TiO_2 has been grown on a glass substrate at laser energy 800 mJ and under vacuum, which is in accordance with the findings of other works Sarmad, et al. (9).

The X - ray fluorescence measurements for TiO_2 pure sample reveal the following weight of percentage 80 % of Titanium and 20 % of O_2 as shown inFig.(4 - a).This reveals the two peaks of both (Ti) and (O2) which are the main constructors of the deposited material. The TiO_2 doping with 5% noble metal (Pt) is clear from Fig.(4-b) that was the weight of percentage of Ti remind at 80 % while the O_2 percentage reduce to 15% and the noble metal a pear at percentage of 5% .

The substrate temperature (Ts) plays an important role in determining the structure of TiO_2 thin films which are fabricated on silicon substrate. Fig.(5) shows the XRD measurements results of TiO_2 film formed at substrate temperatures of 400°C pure TiO_2 on silicon substrate (at laser energy 800 mJ). The deposits at the higher substrate temperature at 400 °C by nanosecond ablation , TiO_2 thin film compound mainly consist of polycrystalline phases with increasing crystalline quality .Fig.(5) the XRD patterns of the TiO_2 films prepared on Si (111) at substrate temperature (Ts =400) °C. The rutile phase appear at 2θ=27.6° (110), because the change of TiO_2 phase transformation from anatase to rutile occurs at temperatures higher than 400 °C under vacuum. which is in accordance with the findings of other works T. Ivanova, et al. (10).TiO_2 films doped with noble metal (Pt) at percent (5%)400°C substrate temperature and 800 mJ laser energy on Si (111) wafer are shown in Fig.(5). At 5% concentration, the film shows diffraction peaks located at 2θ=25.28° and 2θ=32.8°, which belong to anataseand rutile A (101) and R(100) peaks respectively, according to standard pattern of anatanse TiO_2 .

TiO_2 has been grown on silicon (111) at constant laser energy 800 mJ. Fig.(6-a) shows the SEM micrograph of the TiO_2 thin film prepared at temperatures of (400)ºC.TiO_2 thin film have a quite uniform and hole-free surface. At (400) ˚C a homogeneous surface morphology is observed in the film with a wide size distribution of the particles and average particles size is about (25-80 nm). When substrate temperature increases, average size of aggregated particles grows, at the substrate temperature 400°C particle size increase reaches 80 nm obviously.

SEM image of the TiO_2 dopant with noble metal sample is presented in Fig. (6-b) for film deposited at fixed substrate temperature of 400 ºC at 800 mJ laser energy. The film is homogeneously distributed fine pores in all the coatings. The pore size was observed to increase with increasing dopant atom radius. It can be seen that the highly crystalline spherical particles were nanostructures. It is seen in Fig. (6-b) that the nanostructure has a certain type grains and also the voids take place between the grains. It is also found that the metal atoms are diffused into the TiO_2 grains. The pore size was also related to the size of the metal doped into TiO_2. As the size of the metal atoms becomes bigger about (130 x 10^{-3} nm) for Pt atom the pore size increases. The grain size decreases when TiO_2 doping with noble metal, which is in accordance with the findings of other works D. K. Pallottiet et al. (11).

TiO_2 has been grown on wafer silicon (111) at constant 800 mJ laser energy. The surface morphology of the TiO_2 thin films as observed from the AFM micrographs proves that the grains are uniformly distributed within the scanning area (10 µm x 10 µm), with individual columnar grains extending upwards The AFM is one of the most widely used tools for imaging, measuring, and manipulating samples at the nanoscale range. Fig.(7) and Fig.(8) shows 2D and 3D AFM micrograph of the PS layer formed on the p-type Si samples for Pure TiO_2 and noble metal 5% Pt respectively , which is in accordance with the findings of other works K. Z.Yahya et al. (12).

The RMS roughness increase with noble metal percent due the presence of the fine dispersed phase. These samples are very rough with RMS values (52 &58 nm) for thin films doping with (Pure TiO_2&5% Pt) respectively as shown in Table 1 which is in accordance with the findings of other works L. sun et al. (13).

The electrical properties of semiconductor polycrystalline depend on many factors such as temperature, light, magnetic field, density of atoms, and the impurity of the material. However, the study of these properties is very important to predict the electrical conductivity, the quality of charge carriers and thus their suitability to make electronic devices of various kinds, can be determined. The most important electrical examinations depend on the method of the four probes called Van Der Pauw technology that has been used in these tests. Tests are also functions of the electrical conductivity and the concentration of carriers as volumetric and surface carrier's mobility and Hall coefficient in addition to some other important parameters .The findings have shown that a greater increase in the value of electrical conductivity is due to the increase in the values of charge carriers with the decrease in the values of both the mobility and Hall coefficient. Hall coefficient maintains a negative sign which has not been changed by the increase in doping concentration which indicates that the electrons are the charge carriers and responsible for increasing in conductivity, as shown in Table 2.

Capacitance - voltage is important, since it determines different parameters such as built- in potential, junction capacitance and junction type. Fig.(9-a) and (9-b) show the variation in junction capacitance with reverse bias voltage in pure TiO_2 and with noble metal (5% Pt) . These figures show that junction capacitance decreases with increased reverse bias voltage, this behavior is due to an increase in the width of depletion layer with increase reverse biased voltage.

Current - voltage characteristics for pure TiO_2 and 5% Pt doped TiO_2 are shown in Fig.(10) respectively. The produced thin films in this study have been deposition by PLD. Both pure TiO_2 and 5% Pt doped TiO_2 graphs show TiO_2 films deposited on silicon substrate at substrate temperature at 400 ^{o}C and 800 mJ laser power, which is in accordance with the findings of other works S.Aksoy and Y. Caglar ,(14).

4- CONCLUSION

The Present work has reached to the following conclusions:-

1- The x-ray diffraction investigation showed that the structure of TiO_2 film was polycrystalline with synthesis tetragonal.
2- The best transmittance of TiO_2 film is (80%) at thickness 200 nm, within wavelength range (300 – 1100 nm).
3- TiO_2 films have low conductivity and the d.c. electrical conductivity (σ_{dc}) increases with doping 5% Pt .
4- The films have hall coefficient, mobility are increasing with doping 5% Pt.
5- The average grain size of TiO_2 thin film prepared at optimum condition was around (60 nm).

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Table 1 Structural and morphological characteristics of the TiO_2 Pure films deposited with noble metal doping 5% Pt at 400 °C substrate temperature and 800 mJ laser energy.

sample	X-ray of plane grain size (nm)	AFM of plane grain size (nm)	RMS roughness (nm)
TiO_2 Pure	15.247	16.5	2.1
TiO_2 : 5% Pt	8.772	17.28	2.22

Table 2 The result of electrical measurement for pure TiO_2 and doped TiO_2 : 5% Pt films.

sample	μ_H (cm^2/v.s)	σ (Ω.cm)$^{-1}$	n (cm)$^{-3}$	Carrier type	R_H (cm^2/C)
TiO_2 Pure	73.35	$3.279 * 10^{-1}$	$1.503 *10^{11}$	n	$-1.279 * 10^5$
TiO_2 : 5% Pt	17.41	$4.813 * 10^{-1}$	$2.050*10^{11}$	n	$-4.566 * 10^4$

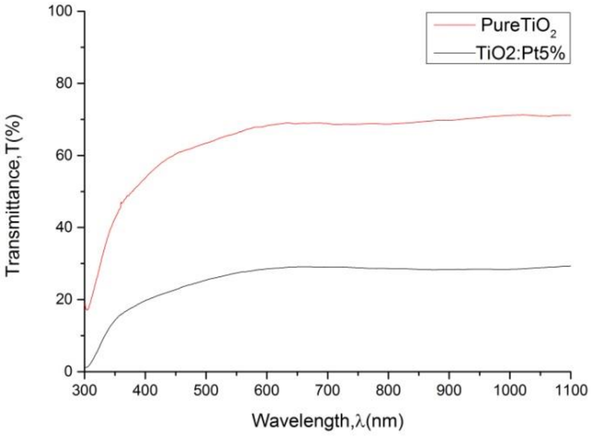

Fig.(1) Optical Transmission as a function of wavelength for TiO_2/ glass at constant temperature (400) ◦C and 5% Pt : TiO_2.

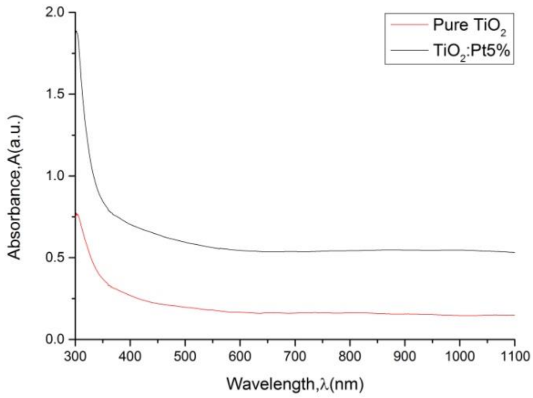

Fig. (2) Optical Absorption as a function of wavelength for TiO_2/ glass at constant temperature (400) ◦C and 5% Pt : TiO_2.

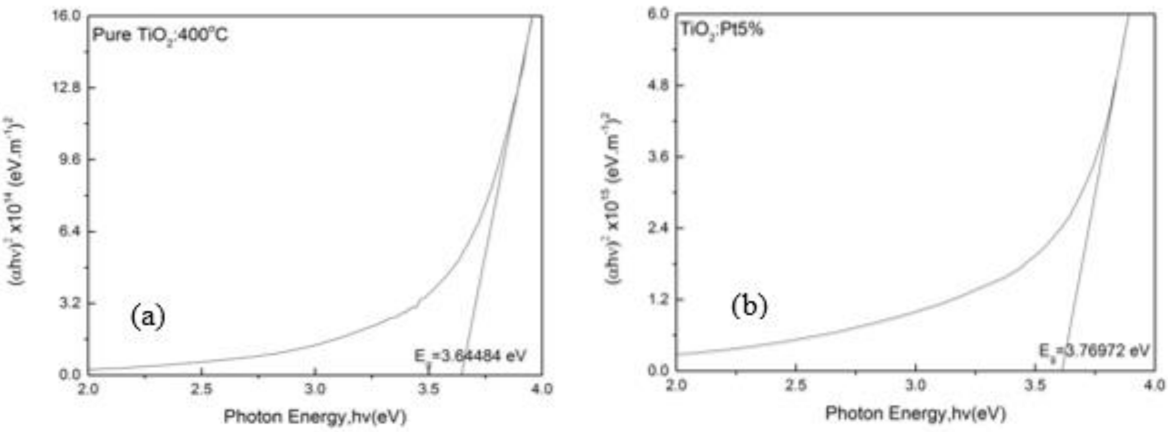

Fig. (3)A plots of $(\alpha h\nu)^2$ verses photon energy (hν) of TiO_2 thin films with constant temperature (a) (400) ◦C and (b)5% Pt : TiO_2.

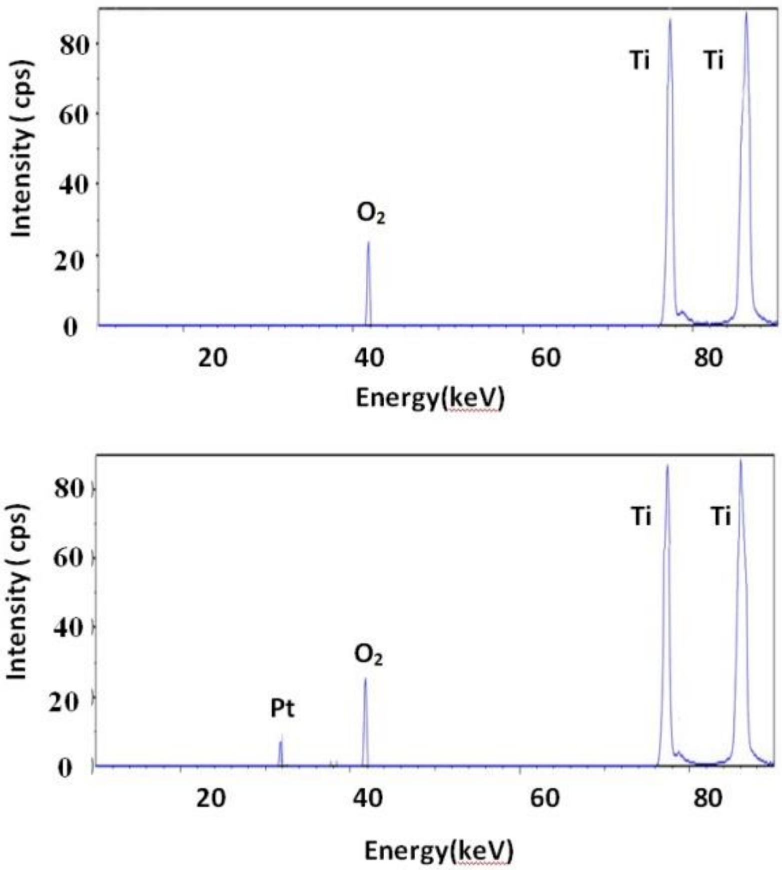

Fig. (5) XRD spectra of TiO_2/Si for TiO_2 pure and 5% Pt : TiO_2.

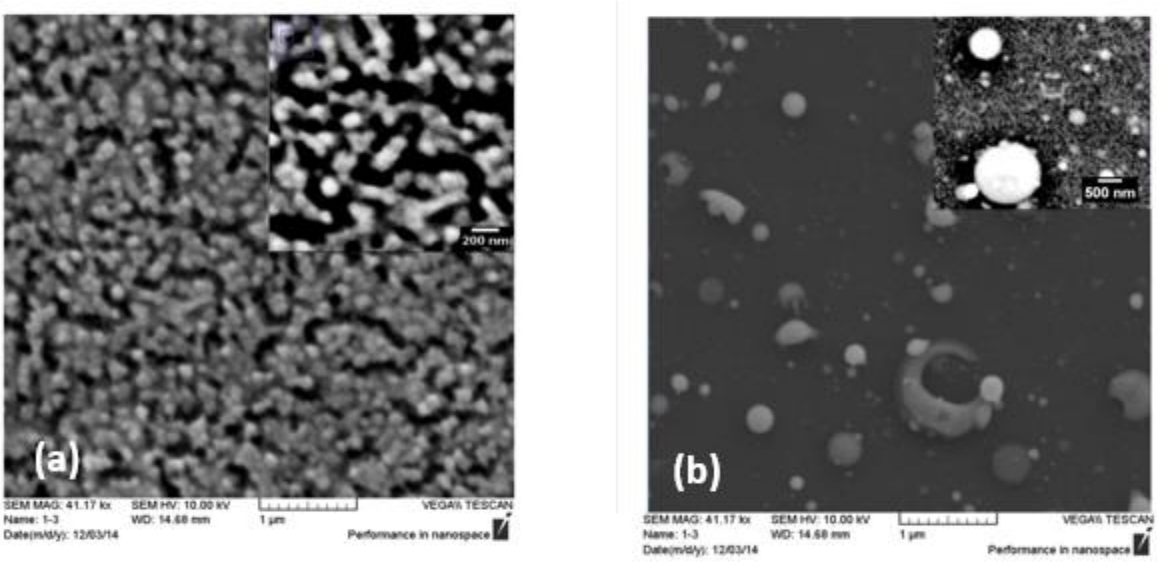

Fig. (6) SEM image of the TiO_2/Si thin films deposited at (a) TiO_2 pure and (b) 5% Pt: TiO_2 laser energy 800 mJ.

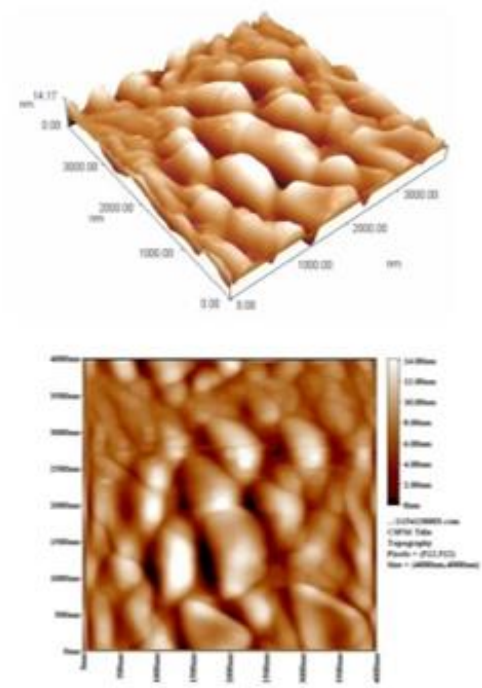

Fig.(7) 2D and 3D AFM image of the TiO_2/Si thin film pure.

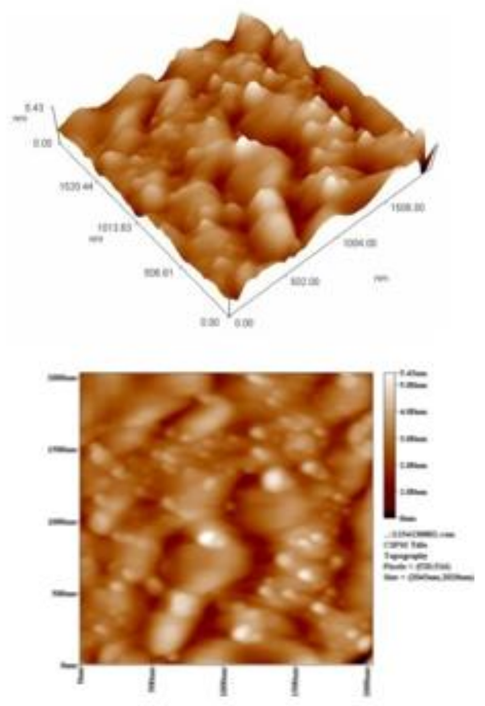

Fig.(8) 2D and 3D AFM image of the TiO_2/Si thin film doping with noble metal 5% Pt .

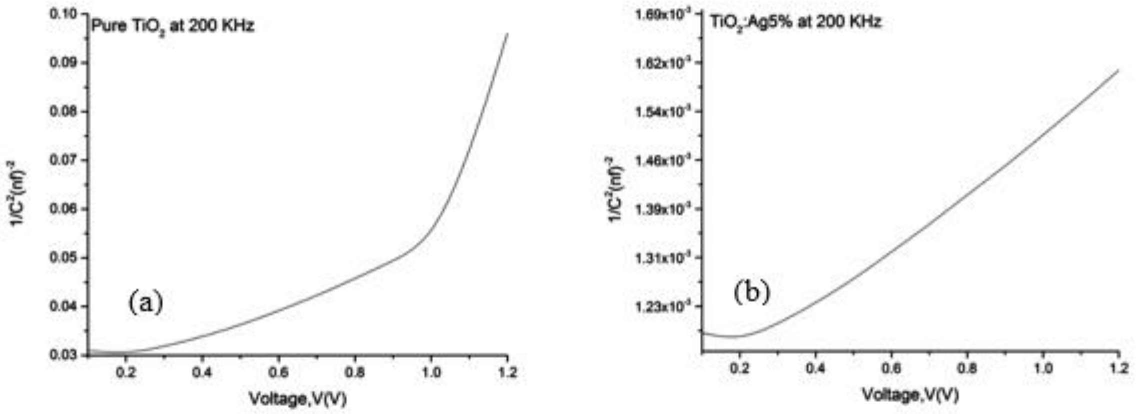

Fig.(9) A plots of $1/c^2(nf)^{-2}$ and V(volt) of (a) Pure TiO_2 thin films and (b) noble metal doping 5%Pt with substrate temperature 400 °C at 800 mJ laser power .

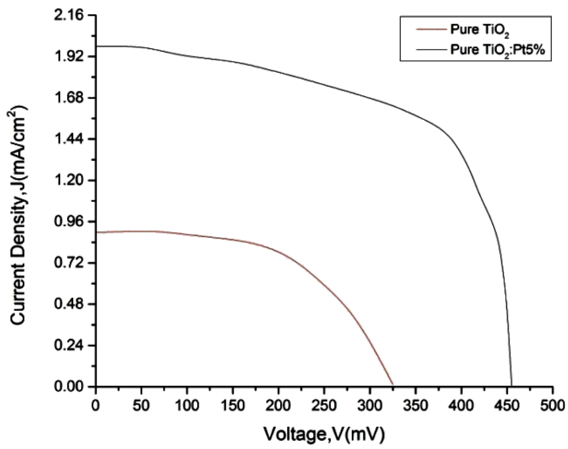

Fig.(10) I-V characteristics of the TiO_2/Si thin film for Pure TiO_2 and doping with noble metal 5% Pt.

ترسيب اغشية ثاني اوكسيد التيتانيوم النقية والمشوبة بمعدن البلاتين باستخدام تقنية التشويب بالليزر

الخلاصة

في عملنا هذا ، تم ترسيب اغشية ثاني اوكسيد التيتانيوم النقية والمشوبة بمعدن البلاتين على قواعد من الزجاج والسليكون عند درجة حرارة C ◦(400)وعند طاقة ليزر m J (800)وبأستخدام ليزر نادميوم ياك النبضي ذو الطول الموجي nm (532) ويعمل بتقنية عامل النوعية ذو معدل تكرار (6 Hz) وامد نبضة (10 nm) وتم دراسة الخواص البصرية بواسطة قياسات مطياف النفاذية للاشعة المرئية والفوق البنفسجية وكذلك تم دراسة الخواص التركيبية لثاني اوكسيد التيتانيوم النقي والمشوب حيث تم استخدام حيود الاشعة السينية (XRD) ومجهر القوى الذرية (AFM) لدراسة الاطوار والحجم الحبيبي للجسيمات النانوية وتم دراسة طبوغرافية السطح بأستخدام المجهر الالكتروني الماسح (SEM) وايضاً تم دراسة الخواص الكهربائية ومنها الموصلية الكهربائية (σ_{dc}) ومعامل هول (R_H) و(C−V) (I−V) وقد اظهرت النتائج وصول النفاذية البصرية الى حوالي(80%) وقد بلغت فجوة الطاقة البصرية (3.64)eV لاغشية ثاني اوكسيد التيتانيوم النقي و(3.76)eV للمشوبة بمعدن البلاتين ، وكذلك تم الحصول على تركيب نانوي منتظم ومتجانس وعند حجم حبيبي نانوي اقل من (20 nm) .