Preparation of NanostructureTiO_2 at Different Temperatures by Pulsed Laser Deposition as Solar Cell

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ABSTRACT

Deposition of the Titanium oxide (TiO_2) particles on glass and the Si substrates was materialized for a wide range of temperatures (100-400) °C; using PLD technique at constant laser energy 800 mJ of frequency doubled Nd: YAG laser wavelength of 532nm running at 10 Hz rate and 10ns duration pulses. UV-Vis spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), Scanning Electron Microscopy (SEM), Atomic Force Microscope (AFM), electrical conductivity (σ_{dc}), Hall coefficient (R_H) and (I-V) and (C-V) measurements were employed to examine optical, morphological and electrical properties of the deposited films. 85% film transparency was accomplished with optical band gap of (3.25 – 3.64) eV. (I-V) characteristics showed an enhanced TiO_2 p-n junction thin film solar cell efficiency by 1.6% at 400°C.

Keywords: Q-switched Nd: YAG laser, morphology, electrical properties, nano-structure, TiO_2

تحضير تراكيب نانوية لثنائي اوكسيد التيتانيوم عند درجات حرارة مختلفة بطريقة الترسيب بالليزر النبضي كخلية شمسية

الخلاصة

تم ترسيب اغشية ثاني اوكسيد التيتانيوم النقية على قواعد من الزجاج والسليكون عند مدى من درجاتالحرارة C ° (100-400) وعند طاقة ليزر J m (800)وبأستخدام تقنية الترسيب بالليزر النبضي ذو الطول الموجيnm (532) ويعمل بتقنية عامل النوعية بمعدل تكرارية (6Hz) وامد نبضة (10ns) وتم دراسة الخصائص البصرية بواسطة مطيافيةالاشعة الفوق البنفسجية - المرئية وتحويلات فورير لمطيافية المنطقة تحت الحمراء (FTIR). كذلك تم دراسة الخواص التركيبية لثنائي اوكسيد التيتانيوم النقي من خلال 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 الخصائص الكهربائية ومنها التوصيلية الكهربائية (σ_{dc}) ومعامل هول (R_H) وسعة –جهد (I-V) وقياس سعة - جهد(C-V) .اذ اظهرت النتائج وصول النفاذية البصرية الى

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حوالي(85%) وبلغت فجوة الطاقة البصرية (3.64 - 3.25) eV. وأظهرت نتائج الخصائص الكهربائية للاغشية المحضرة عند درجة حرارة (400°C) زيادة في كفاءة الخلية الشمسية بمقدار (1.62 %) .

INTRODUCTION

Alternative energy sources like Solar cells have drawn the attention in recent decades due to the enormous energy obtained by earth from the sun; about 1.2 × 1017W. The potential of the solar cells is focused to replace fossil fuels as the main means of electric power generation. Solar cells of all types suffer from two main deficiencies: relatively low conversion efficiency and high cost in comparison with conventional fossil fuel electric sources [1]. Interests towards the Nanostructured titanium dioxide (TiO_2) was grown in the past decades, due to its interesting physical and chemical properties, as well as the great potential applications in a wide range of fields including catalysis, photo-catalysis, photoluminescence, solar cells, fuel cell, and gas sensor [2–5]. The attractive physical and chemical features of TiO_2 depend on the crystal phase, particle size, and also on the particle shape. For example, varying crystallinity of TiO_2 leads to different band gaps: rutile TiO_2 of 3.0 eV and anatase TiO_2 of 3.2 eV, which determine the photo-catalytic performance of TiO_2. Besides; particle size plays an important role in nano-crystalline TiO_2 based catalysts. Small particles offer a large surface area and exhibit high photo-catalytic activity; mostly by influencing the dynamics of e^-/ h^+ recombination and the adsorption rate and adsorbed amount of reaction species [6,7,8]. TiO_2 thin films had been synthesized by numerous methods including plasma oxidation [9], chemical vapor deposition(CVD) [10], metal organic chemical vapor deposition (MOCVD)[11], sputtering [12], atomic layer deposition (ALD) [13], plasma-enhanced ALD (PEALD) [14] and pulsed laser deposition (PLD) [15,16,17]. Among those techniques, PLD provides thin films with good mechanical rigidity and high specific surface area [18, 19]. In this technique, the stoichiometry of the films deposited by PLD method is similar to that of the bulk target used for ablation. During ablation, oxygen may be lost and this necessitates maintaining the oxygen partial pressure in the chamber to obtain stoichiometric oxide films. TiO_2 thin films fabricated by pulsed laser deposition have previously been studied by various research groups [20–25]. In the present work, the fabrication of nanostructured TiO_2 thin films is presented using PLD laser deposition on heated silicon substrates under vacuum conditions. Pulsed laser deposition (PLD) is a humble and low cost method to grow oxide films under different deposition conditions which result in different structural and electrical films' properties.

Experimental Work

Two different types of substrates were utilized for depositing thin films by laser ablation. These are (1 x 2) cm^2 glass plates and 1 cm^2 square-shape p-type silicon substrates of (1.5^{-4}) □cm resistivity at (111) orientation. The PLD experiment was carried out inside a vacuum chamber at (10^{-4} Torr), of O_2, N_2 and Ar background gases. The frequency doubled 10 Hz, 10 ns, 800mJ Nd: YAG laser was focused on the target surface at 45° angle of incidence at different temperatures (100 – 400) °C and using 100 laser pulses. The surface morphology of the films was tested using structure and optical microscope. The transmittance of the films was checked in spectral range (300–1100) nm using UV-VIS (SP8001) Shimatzu double beam spectrophotometer. The crystallinity of the obtained films was studied using XRD and XRF Shimatzu (6000) using CuKa radiation. Additionally, the crystalline structure was studied with (Philips) FTIR system using CuKa radiation. Characterizations of these films were studied by Atomic Force Microscope AFM (Shimatzu AA3000 Scanning probe Microscope).

Results and Discussion

The optical transmittance and absorbance of the TiO_2 films on glass; prepared by PLD, was measured by using UV-Vis spectrophotometer. For film preparation, 800 mJ of laser energy was used to obtain 150 nm films' thickness. The UV- Vis optical properties in the range (300 – 1100) nm at various temperatures (100- 400) ºC showed temperature dependent transmittance and absorbance, as shown in figures (1 and 2). The average TiO_2 film transmittance was found to go beyond 80% in the near-infrared zone. This indicates that TiO_2 films can be used as a window material for solar cells. All films showed a slight decrease in optical transmittance at higher temperatures. This is attributed to the surface roughness increase because of crystallite densification and agglomeration at higher temperatures which led to higher surface scattering [26]. Figure (2) shows that TiO_2 films absorbance increases with increasing substrate temperature. This is probably due to the increased particle size and surface roughness, and also to the phase transformation from anatase to rutile which results in band gap decrease.

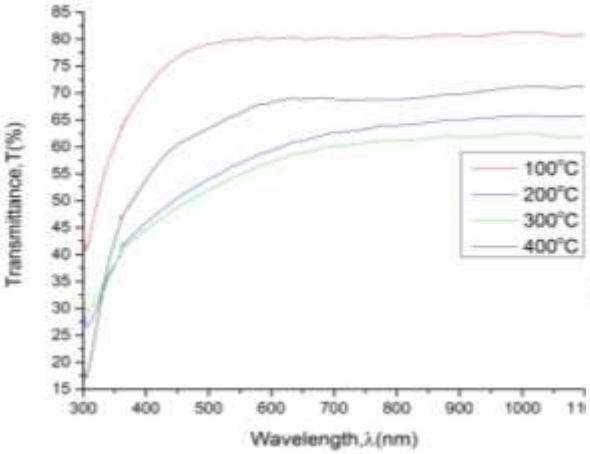

Figure.(1) Optical Transmission as a function of wavelength for TiO_2/ glass at different temperatures between (100 – 400)˚C

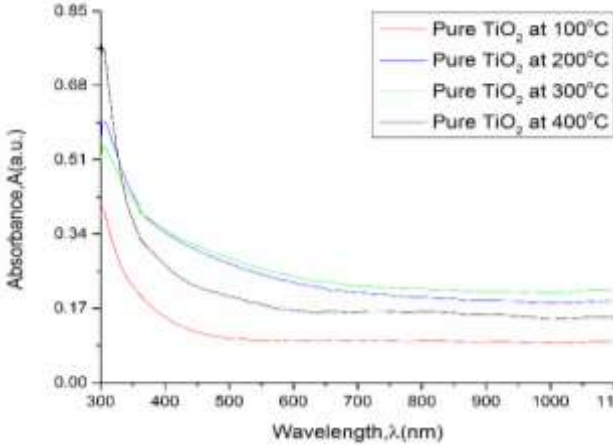

Figure.(2) Optical Absorption as a function of wavelength for TiO_2/ glass at different temperatures between (100 – 400) ◦C

The optical band gaps were measured by plotting $(\alpha h\upsilon)^2$ verses $h\upsilon$ for TiO_2 films and are illustrated in Fig.(3). The band gap values: (3.65, 3.31, 3.25 and 3.64) are corresponding to the (100,200, 300 and 400) ◦C temperatures and are greater than the TiO_2 bulk due to the particle size reduction caused by quantum confinement and upsurge of surface/volume ratio. The surface atom had lesser coordination number and the atomic interaction may raise the highest valance band energy and declines the lowest unoccupied conduction energy band. This allowed the band gap energies to grow. High absorption coefficient has resulted for the rutile TiO_2 thin films which showed direct band gap. The simplicity of rutile TiO_2 thin-film deposition at room temperature is useful for direct fabrication of extremely thin absorber (ETA) solar cells and dye-sensitized solar cell [27].

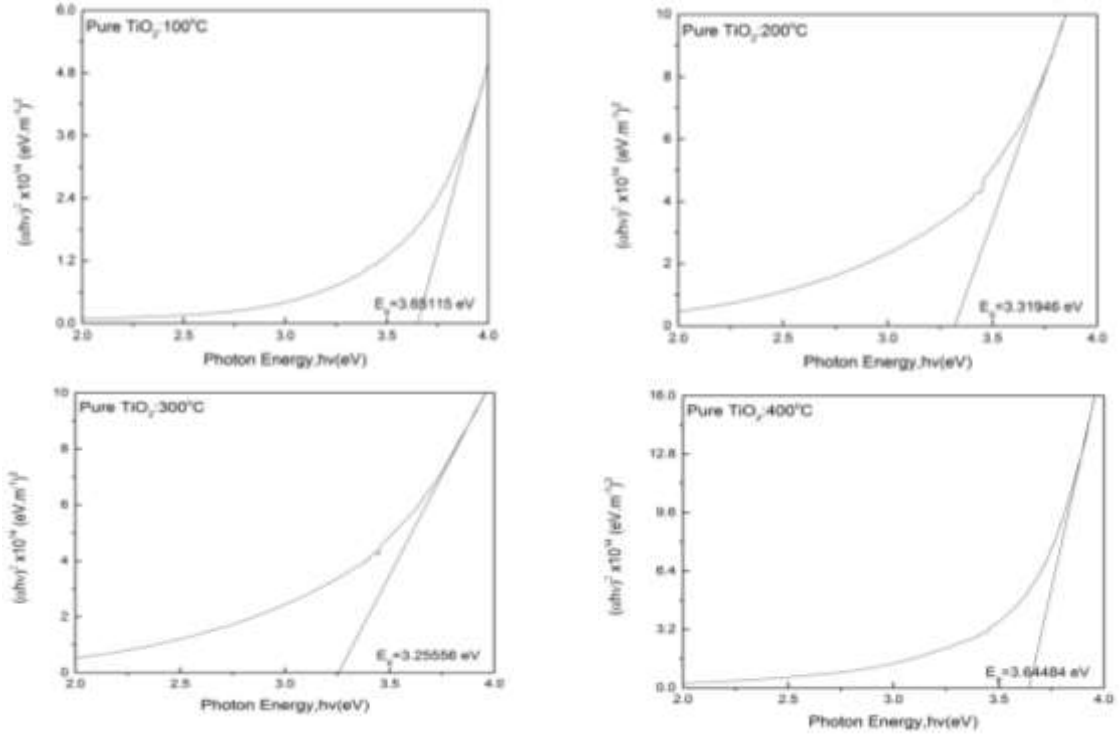

Figure (3)A plots of $(\alpha h\nu)^2$ verses photon energy (hv) of TiO_2 thin films with different substrate temperature a)100 °C, b) 200 °C , c)300 °C and d) 400 ° C.

The substrate temperature (T_s) plays an important role in determining the structure of TiO_2 thin films; fabricated on silicon substrates. Figure (4) shows the XRD results for different TiO_2 films formed at substrate temperatures of 100°C, 200° C, 300 °C and 400° C on silicon substrates using 800mJ of laser energy. Diffraction peaks are located at 2θ=28°, 2θ=48.1° and 2θ=55.6°. It can be seen that the films are amorphous at T_s = 100 °C. When T_s rose to 200°C diffraction peaks were located at 2θ=39.05°, 2θ=40.89° and 2θ=53.68° which correspond to the R (200), R (111) and A (105) peaks respectively. When the temperature rose to 300°C, the diffraction peaks were located at 2θ=38.94°, 2θ=40.81° and 2θ=53.57° which correspond to the R (200), R (111) and A (105) peaks respectively. Films deposited at Ts = 300 °C and Ts = 400 °C are completely polycrystalline. Figure (4-2) shows dominant peaks at 2θ =35.67°, 2θ=38.93°, 2θ =40.70° and 2θ=53.50° corresponding to R (101), R (200), R (111) and A (105) peaks respectively. The peak intensities increased with increasing substrate temperature which also arrowed the peaks' Full Width at Half Maximums (FWHM) and increased the grain size. Higher substrates' temperature led to a decrease in the nucleation density and a smaller number of centers started to develop which enhanced the grains.

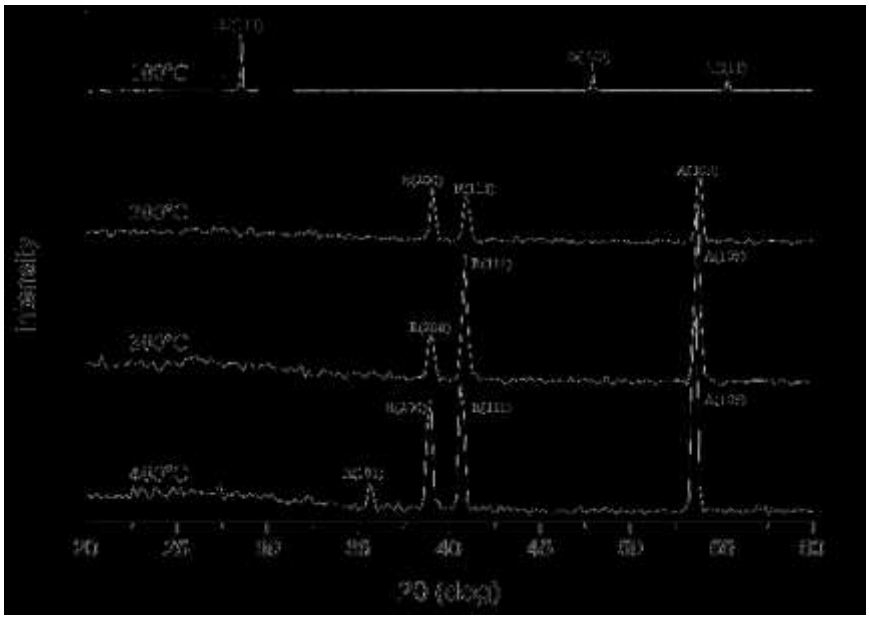

Figure (4) XRD: spectra of TiO_2/Si at different temperature

a) 100◦C b) 200◦C, c)300◦C and d) 400◦C

It is clear that the crystalline size at low temperature is lower at (100 and 200°C) compared to that at high (300 and 400°C) and increases with increasing of Ts. The structure of TiO_2 in XRD investigation is anatase, rutile and brookite titanium dioxide. The substrate temperature is an important element in determining the crystal composition of the multi-crystalline materials particularly nanoparticles compositions during the increase or decrease of the grain size. The later increases the crystallization of the material, the loss of defects and the production of atoms inside the material; in order to produce sufficient energy to re-arrange itself within the crystal lattice. The chemical structure of the TiO_2 thin films were investigated using Fourier Transform Infrared (FTIR) spectroscopy. Fig (5) displays the spectrum of the TiO_2 thin film. The broad peak at 3100–3600 cm^{-1} is allocated to the fundamental stretching vibration of hydroxyl group (free or bonded) [2]; Ti-OH in our study. A weak band at 1624 cm^{-1}[3] is related to the bending vibration of coordinated H_2O, as well as Ti-OH [4]. The broad band below 1000 cm^{-1} (include minima at 754, 583, 522 and 471 cm^{-1}) can be ascribed to characteristic Ti–O and Ti–O–Ti stretching and bending vibrational modes for rutile TiO_2; in accordance with the findings of other published work(**Zhenquan Tan et al)** [8].

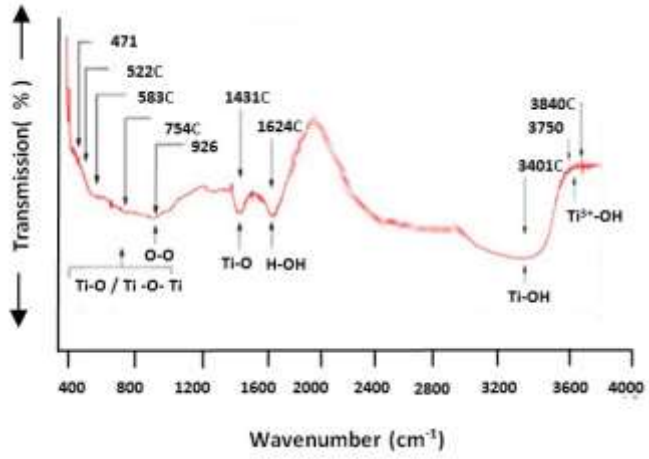

Figure. (5) FTIR spectrum of TiO_2 thin film deposited at substrate temperature=400 °C with laser energy 800 mJ

The x-ray fluorescence tests of the pure TiO_2 sample reveals a weight percentage of 80% Titanium and 20 % O_2 as presented in Fig (6). This indicates the two peaks of both (Ti) and (O_2) which are the main constituents of the deposited material.

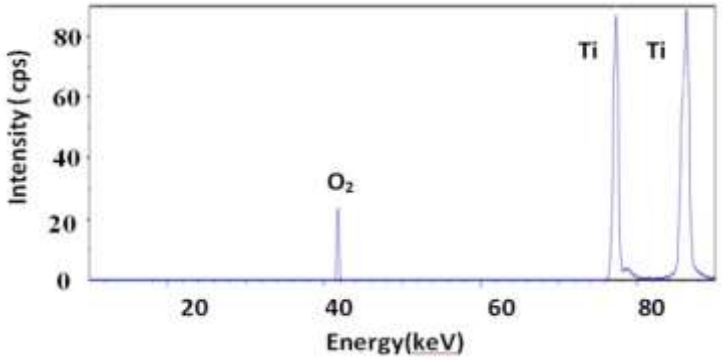

Figure (6): X-ray fluorescence pattern for TiO_2 Pure

The growth results of TiO_2 on (111) silicon at laser energy of 800 mJ are illustrated in Fig (7). These results demonstrate the SEM images of TiO_2 thin films at substrate temperatures (100, 200,300 and 400) ºC. They show quite uniform and hole-free surfaces belong to TiO_2 thin films. The film have homogeneous surface morphology at (100- 400) ◦C, with a wide size distribution of the particles between (25-53 nm). By decreasing the substrates' temperature, the average size of deposited particles increases. As the substrate temperature approaches 400 ◦C, the particle size increases. The AFM images of the pure TiO_2 thin films are presented in Fig (6). Thin films were deposited at different substrate temperatures (100, 200, 300 and 400) ◦C at fixed 800 mJ laser energy. These images show uniform granular surface morphology. An average grain size was evaluated from the plain view images in the range (6-16) nm which is in good agreement with the findings of other works **Khaled Z.Yahya et al** [29].

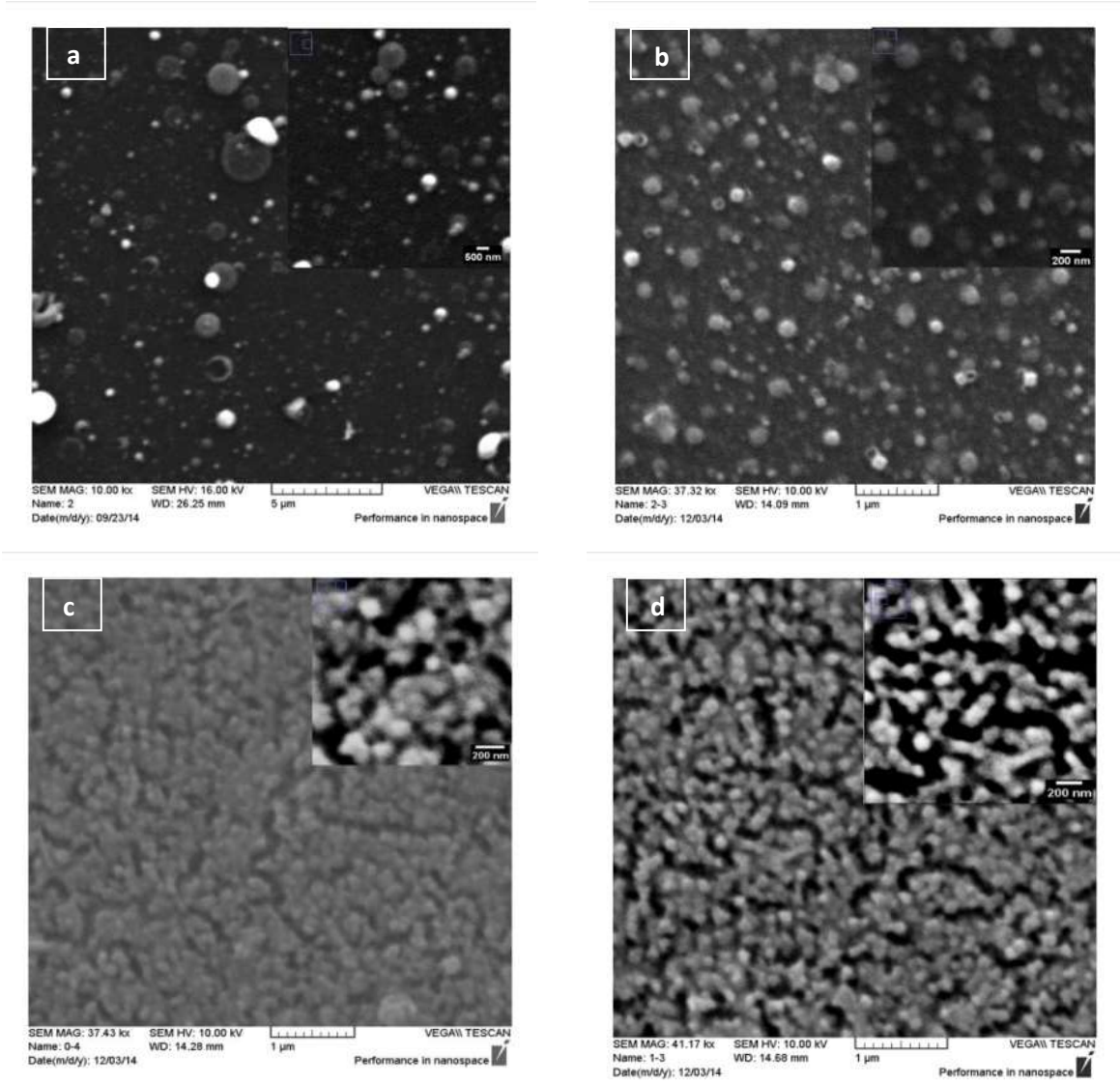

Figure. (7) SEM images of the TiO_2/Si thin films deposited at various temperature of a) 100°C, b) 200°C, c) 300°C, and d) 400 °C at laser energy 800 mJ .

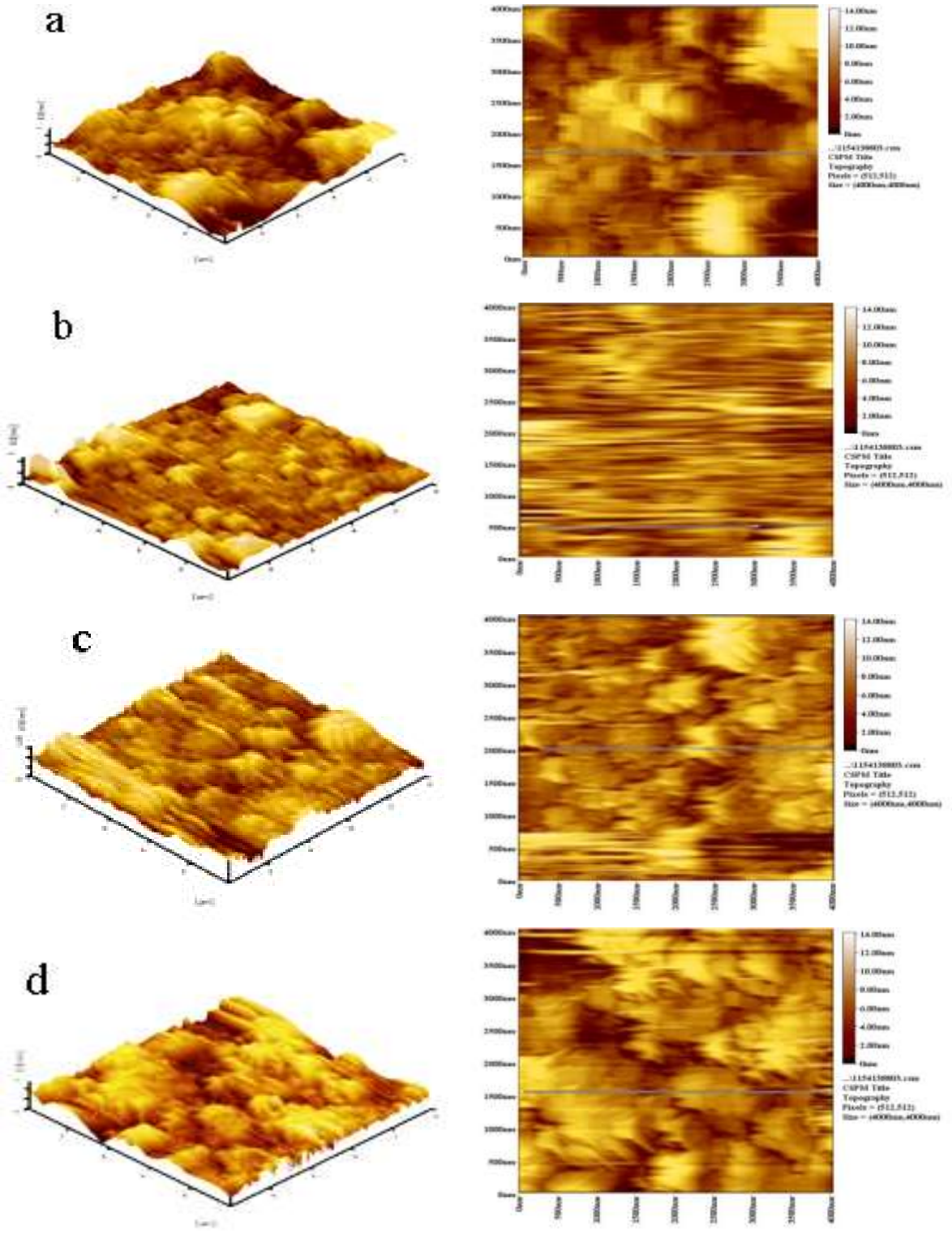

Figure.(8) 2D and 3D AFM image of the TiO_2/Si thin film pure temperature of a) 100°C, b) 200°C, c) 300°C, and d) 400 °C at laser energy 800 mJ .

Electrical properties of polycrystalline semiconductor depend on many factors such as temperature, light, magnetic field, density of atoms, and material impurity. These properties are very important to predict the electrical conductivity and the type of charge carriers; thus, their suitability to make various electronic devices can be determined. Four-point probe Van Der Pauw) was utilized to characterize these properties.

The highest value of electrical conductivity was found to be accompanied by an increase in charge carriers and a decrease in both the mobility and Hall coefficient. Hall coefficient sign has not been changed by increasing the doping concentration. This indicates that the electrons are the charge carriers which are responsible for the increased conductivity, as shown in Table 1.

Table 1: The result of electrical measurement for pure TiO_2

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**	**$-1.279 * 10^5$**

C–V measurements are significant to determine the built-in potential, junction capacitance and junction type. Fig (9) and Fig (10) display the variation in the junction capacitance with reverse bias voltage in pure TiO_2. This demonstrates a decreasing junction capacitance with reverse bias increase. This behavior is due to the increased depletion layer width with the increase of reverse biased voltage.

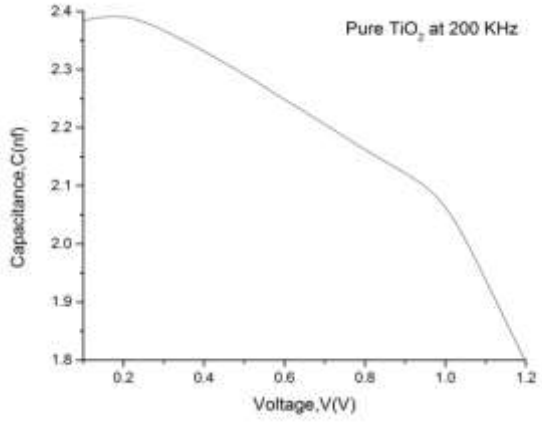

Figure (9) A plot of C(nf)and V(volt) of TiO_2 thin film

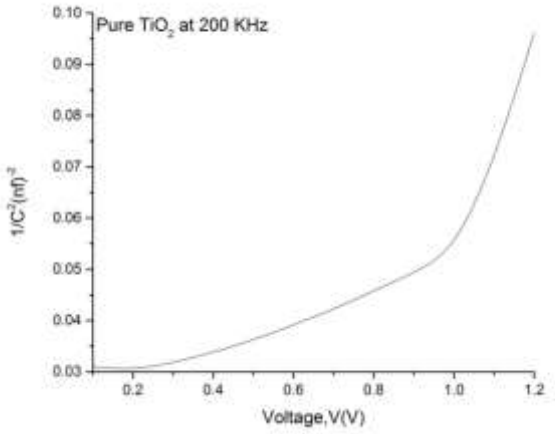

Figure (10) A plot of$1/C^2(nf)^{-2}$and V(volt) of TiO_2 thin film

The solar cell factors in Table 2 demonstrate an enhanced efficiency by 1.26% for Pure TiO_2 thin films. I-V characteristics of these pure TiO_2 thin films are shown in Fig (11). The obtained data

exhibit that this TiO_2/p-Si heterojunction nanostructure can be considered as a good candidate to manufacture semiconductor devices; in agreement with the findings of **SevalAksoy** [9].

Table 2 parameters of the solar cell of Pure TiO_2

Monocrystalline black solar cell
Efficiency : 1.26 %
Max. voltage (V_{max}): 275 mV
Open circuit voltage (V_{oc}) : 325 mV
Max. current (I_{max}) : 0.6 mA/cm^2
Short circuit current (I_{sc}) : 0.90 mA/cm^2
Dimensions: 15×15×2.8 mm

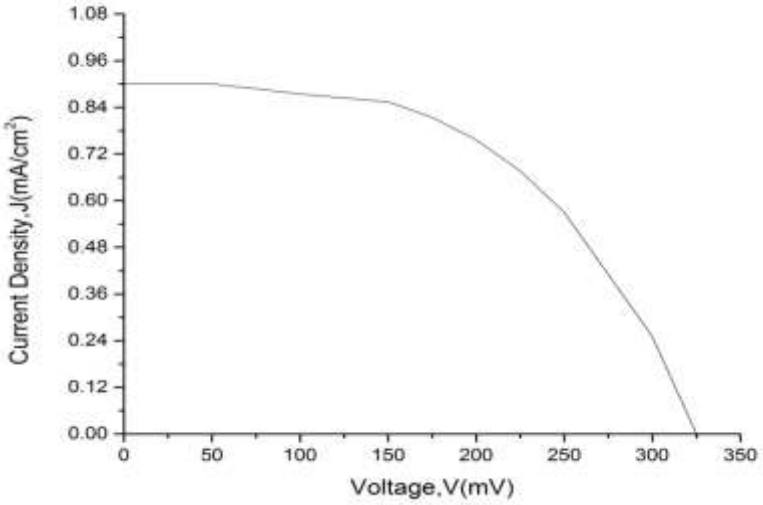

Figure.(11) I-V characteristics of the TiO_2/Si thin film for Pure TiO_2 .

CONCLUSION

In this work we fabricated highly conducting nanostructure titanium oxide thin films as solar cells, using pulsed laser deposition technique at different substrate temperatures. The optimum conditions were met at 400^{o}C. At this temperature, the transmittance was about (65%), energy gap (3.64 eV) and electrical conductivity (3.279 * 10^{-1} (Ω.cm)$^{-1}$). These optimal data have pushed the solar cell efficiency 1.26% higher than its original value.

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