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Structural, Optical, and Electrical Characteristics of Titanium Dioxide Thin Films Prepared by Pulsed Laser Deposition

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Abstract

In this research, the Pulsed Laser Deposition (PLD) technique was used, and the operating frequency of the laser was tuned to a double frequency. This was done in order to construct nano-thin films of titanium oxide (TiO_2). An Nd-YAG laser with a wavelength of 1064 nm, pulse frequency of 6 Hz, and laser energy of 700, 800, and 900 mJ were used on glass and Si (p-type) substrates of different thicknesses. Then, the TiO_2 films were annealed for 2 hours at a temperature of 400 °C. UV-Vis spectra revealed that TiO_2 has strong UV absorption, as well as a large energy gap (2.9, 3.06, and 3.3) eV for energy levels (700, 800, and 900) mJ in contrast. In addition, FESEM analysis showed a granular morphology that showed a tendency for fragmentation into smaller particles with the growth of the thickness of the sample. The thickness of the thin films was determined using the FESEM cross-section, and the results showed that the thicknesses were 278.01, 1630.53, and 2579.66 nm for TiO_2 at laser energy of 700, 800, and 900 mJ, respectively. As the laser energy increased, the results showed an increase in the thickness of the thin film. In addition, the absorbance increased while the transmittance decreased with increasing thin film thickness. In terms of the electrical properties of the cell, we found that the efficiency of the annealed cell was significantly increased compared to that of the unannealed cell.

1. Introduction

In most nations, a person's way of life depends on the availability of facilities that keep up with the advancement of various aspects of our lives, including technology and energy. Where individuals always aspire to improve their lives, the accessibility and efficient use of energy make life more comfortable. The majority of the energy utilized by nations comes from fossil fuels including coal, oil, and gas. They cannot, however, be easily acquired. Furthermore, if these kinds of raw fuels are not transformed into consumable goods, they are no longer valid for usage. The production of fuel results in pollution of the surrounding environment and contributes to the warming of the planet. Warming of the planet's atmosphere is widely recognized as one of the most dangerous effects of human activity [1].

As a result, there will be an increase in emissions produced and released into the atmosphere, which will cause extremely dirty weather. Researchers are constantly seeking new energy sources that don't emit any emissions while they are operating because of the pollution problem. The energy sector is being pushed to identify sources of sustainable energy for yet another reason. The sun is the finest potential energy source to supply all users on the planet with electricity. Solar energy, often known as sun-based energy, is a type of renewable energy that is good for the environment and has attracted the attention of a significant number of scientists and researchers from all over the world [2]. Two distinct forms of energy can be generated through the utilization of solar radiation. Photovoltaic cells, also known as PV cells, are the ones responsible for the transformation of light into electricity, whereas thermal energy sources are the ones that convert sunlight into heat [3, 4].

There are many methods for preparing thin films as a result of the expansion of their applications and uses. The appropriate method for the different nature of the raw materials used in terms of their melting and evaporation, the occurrence of decomposition of the substance, the type of substrates on which the films are deposited, and the development of science and technology in thin film production [5]. Preparation methods have become a high degree of accuracy in terms of determining the thickness and homogeneity of the film. Preparation methods are divided into two types: physical methods and chemical methods [6].

Pulsed laser deposition one of the important methods of deposition of thin films is the pulsed laser deposition technique, which is considered as the most important methods for the growth of thin films. This technique includes three main parts: the chamber, the laser, and the vacuum system. The pulsed laser deposition method represents one of the simpler methods because it does not require equipment of a complex nature to prepare thin films of different materials, as this method leads to the formation of nanoparticles of a Nano size ranging between 10-100 nm [5, 6]. TiO_2 Extensive research into this material has led to the discovery of a wide variety of fascinating applications for TiO_2. These applications may be found in sectors as diverse as photovoltaics, photocatalysis, photo-electrochromics, and sensors. These applications can be broadly categorized as "energy" and "environmental," and a large number of them depend not only on the properties of the TiO_2 material itself but also on changes in the host that the TiO_2 material is attached to. Solar cells depend on TiO_2 material and temperature [6]. Anatase, rutile, and brookite are the three crystalline forms of TiO_2 that are found in nature. Because anatase has a massive band gap of 3.2 eV and a bigger conduction band edge, it is the preferred crystal structure for dye-sensitized solar cells. As a result of the interaction between these properties, a higher Fermi level and open circuit voltage are produced. The third crystalline form of TiO_2 is called brookite, and it is extremely challenging to make. As a direct consequence of this, dye solar cells do not make substantial use of brookite [4, 6].

Rajaa, et al. (2021) deposited TiO_2 On comparatively flat glass substrates, thin films employing spin coating with many layers. TiO_2 layers produce samples with average particle sizes of less than 4 nm and three-layer gel thin films with maximum lengths of 62 nm due to their good optical and morphological properties. The research results show that all films have low roughness levels [7]. G. H. Mohammed, et al. (2021) studied, the electrical properties of group nano-transition metal oxides, such as (ZnO-TiO_2) thin films. The films were deposited on glass substrates using Nd-YAG laser with 400 pulses, 800 mJ, and 1064 nm. The films' conductivity rose when doped with metal oxides, and the maximum conductivity was achieved when treated according to the type of doped metal oxide. According to Hall Effect investigations, each film has both n and p charge carriers [8]. Joginder, et al. (2022) showed that titanium dioxide (TiO_2) thin films have a wide range of uses, and the various structures of the produced films can result in new or improved features. Several optoelectronic devices, including solar cells, light-emitting diodes, liquid crystal displays, etc.,may use the well-known semiconductor TiO_2 [9]. Sabah .N. Mazhir et al. (2023). This paper investigated ZnO: Fe_3O_4 nanostructure structure and optical characteristics. Pulse laser deposition with a 1064 nm Nd:YAG laser at 500, 600, and 700 mJ produced thin films on glass substrates. XRD, SEM, and AFM demonstrated that ZnO: Fe3O4 had an FCC phase after altering laser energy. AFM scans showed that magnesium immunization enhanced grain size ratio and decreased surface roughness. The thin films' absorption Spectrum and optical energy gap were compute [10].

This work aims to deposit a nanostructure thin films of pure TiO_2 on quartz and Si wafer by using PLD method at laser energy (700, 800, and 900) mJ. Annealing the coated films at 400 ℃ for 2 h. Then, Characterization of the TiO_2 films by using different techniques such as FESEM, XRD, CROSS SECTION, and UV-Vis). Nanostructure solar cell fabrication and measurements (R_S, R_{SH}, V_{OC}, J_{SC}, F, and PCE). Nanotechnology-enhanced solar cell efficiency.

2. Experimental Procedure

2.1. Materials

Table (1). Properties of Materials**.**

Materials	Properties	Company
Wafer Silicon	P-type Resistivity 1-10 Ω.cm 76.200 mm diameter 0.5 mm thickness	Mansour State Company
Titanium oxide	Assay> 99.5%	Thomas Baker
Pure aluminum(Al)	Assay> 99.0%	Thomas Baker
Silver Conductive Paint	5.0 ml	MG chemicals
Copper wire	Electrical Resistivity 1.72 Ω.cm Young Modulus 130GPa	Thomas Baker
Aluminum mask	Thickness 0.4 mm	Mansour State Company

2.2. Target Preparation

Titanium oxide and Zinc oxide powdered were utilized to make the target. For five minutes, a single-axis hydraulic press with a pressure of 92.68 MPa compressed powdery materials into tablets with dimensions of 2.5 cm and 0.4 cm thickness.

2.3. Preparation and Cleaning of Quartz and Si Wafer Substrates

The deposition of films on substrates made of quartz and silicon (p-type) has a 1 cm × 1 cm size. Before using the substrates, it must be cleaned and treated to remove impurities and suspended materials because their presence will affect the created films' optical qualities.

2.4. Deposition Process

After preparing the compressed targets of zinc oxide and Titanium oxide as mentioned previously, they were placed on the target holder. Then a quartz and Si substrate are fixed on the pillar holder at a distance of (12 cm). (Nd-YAG) laser with a wavelength of 1064 nm and a number of pulses of 250 was used, and a vacuum pressure of 10-3 mbar. Laser energy of 700, 800, and 900 mJ and substrate temperature of 300 °C. Table (2) shows the PLD Properties.

Table (2). The PLD Properties.

Laser	Wavelength (nm)	Pulse energy (mJ)	Pulse repetition rate (Hz)	Pulse duration (μs)
Nd-YAG	1064	700 800 900	3	10

2.5. Silicon Back Surface Coating by PVD

The back surface of the silicon wafer (P-Type) was coated using a device (PVD) where the wafer was coated with aluminum A voltage 70 volt and current 1.2 A were applied and under pressure of 1×10^{-4} mbar). The powder was placed in and fixed to the target where a layer of aluminum with a thickness of 100 nm.

2.6. Preparation of Masks and Contact Metallization

The mask that was deposited on the front side of the solar cell was done so with the use of a thermal evaporation. The masks are prepared by thermal evaporation in vacuum pressure (5×10^{-5} mbar). Aluminum wire was wrapped around a Tungsten rod and thermally evaporated by applying (31 volt) to form an electrode thickness of 200 nm of Al mask on the thin film.

3. Results and Discussion

3.1. Field Emission Scan Electronic Microscope (FESEM) with Cross Section

The FESEM was utilized for the study of surface morphology, the thickness of thin films, and the estimation of film thicknesses for films that did not have uniform surface forms based on analytical data. These tasks were carried out using analytical data. As can be seen in Figure (1), it is believed that the surface properties of transparent conductive oxides (TCO) films, which are essential factors for applications in optoelectronic systems, have an effect on the optical properties of the TCO films. This theory is supported by the observation that the optical properties of TCO films are affected by their surface properties. This is the situation with films that were deposited on quartz substrates utilizing the (PLD) method of preparation. To be more specific, when the laser intensity is strong, the films exhibit a certain degree of homogeneity, with some large particles forming from small intergranular fusion processes. According to the findings of the investigation, all of the grown films have a granular morphology that is agglomerated in columns that are perpendicular to the substrate, and they have a tendency to form smaller particles as the thickness increases as shown in Table (3). This was determined despite the fact that the thickness of the films varied.

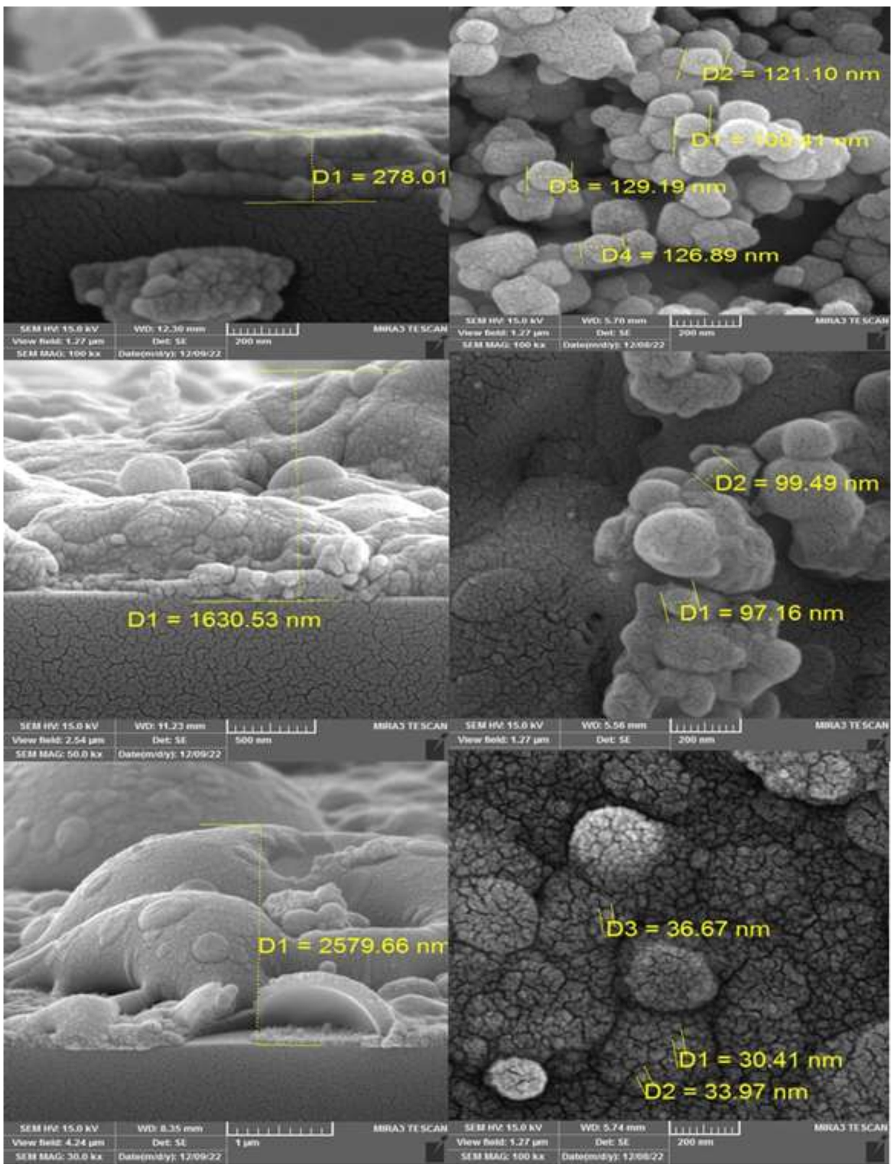

Figure (1). FESEM and cross section for TiO_2 at thickness (a) 278.01nm, (b) 1630.53nm, and (c) 2579.66 nm.

Table (3). Particles dimensions from the FESEM images for the nano-thin films.

Sample thickness (nm)	Size or particles size(nm)
278.01	121.10
	100.41
	129.19
1630.53	99.49
	97.16
2579.66	36.67
	30.41
	33.97

3.2. X-Ray Diffraction (XRD) Analysis

Figure (2) shows XRD patterns of deposition samples to determine their crystalline structure. Those are thin film samples of TiO_2 deposited on quartz with laser energy of 700, 800, and 900 mJ. These patterns showed anatase and rutile TiO_2. Thus, mixed-phase TiO_2 samples were obtained, corresponding to (110), (101), (210) and (211) crystallographic planes. The phase produced like rutile (JCPDS card no. 21-1276). The anatase phase was present since the diffraction peaks at 62.3°, 68.7°, and 53.9° corresponded to the crystal planes of (204), (116), and (105) (JCPDS card no. 21-1272).

The TiO_2 nano-thin films exhibit broadened reflection peaks as a result of the small particle sizes. Without annealing, the average crystal size of TiO_2 it was 17.58, 10.9, and 7.8 nm. When the thickness and laser energy are both increased, the crystal size of TiO_2 nano-thin films virtually decreases. With increasing thickness and laser energy, it can be shown that nano-thin films with polycrystalline structures tend to generate nanoparticles, which is related to tensile stress that may be caused by defects such oxygen vacancies or the production of nanostructures in TiO_2 films. The lattice instability brought on by the flaws leads to the development of intrinsic stress in the films. Due to the fact that the atoms in the lattice have not changed positions, the disorder appears to persist as the thickness increases, and the tensile stress in TiO_2 films is still present at the interfaces where the films and quartz substrate meet.

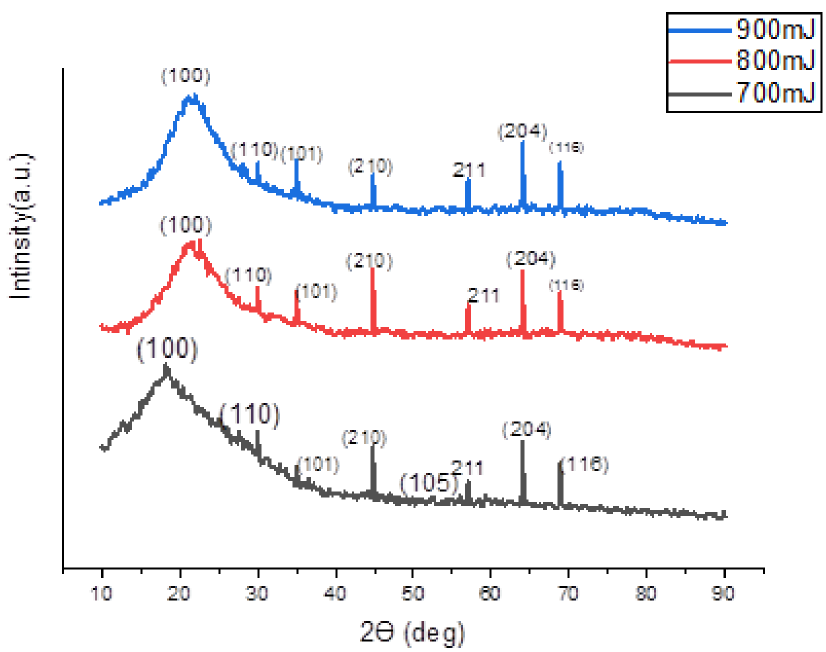

Figure (2). The X-ray Diffraction for samples TiO_2 at 700 mJ, TiO_2 at 800 mJ, TiO_2 at 900 mJ.

Table (4). Information regarding the structure of the XRD pattern for nano-thin films of TiO_2 with varying thicknesses.

Sample	(hkl)	Peak position (2θ)	FWHM β (deg.)	Crystal size D(nm)	Average crystal size (nm)
Sample TiO_2 at 700mJ	(110) (101) (210) (211) (204) (116) (105)	27.5°, 36.1° 44.3° 54.4° 62.3° 68.7° 53.9°	0.142 7.39 5.59 1.131 0.063 0.1814 3.897	0.127 1.545 0.696 53.06 8.033 2.224 57.40	17.58
Sample TiO_2 at 800mJ	(110) (101) (210) (211) (204) (116) (105)	27.5°, 36.1° 44.3° 54.4° 62.3° 68.7° 53.9	3.86 3.98 0.0127 27.2 6.14 5.29 0.052	2.89 3.05 41.244 2.09 1.22 6.76 0.255	10.9
Sample TiO_2 at 900mJ	(110) (101) (210) (211) (204) (116) (105)	27.5°, 36.1° 44.3° 54.4° 62.3° 68.7° 53.9	5.28 4.34 0.057 53.21 0.485 13.9 4.41	1.23 1.73 1.744 1.886 0.126 46.6 1.88	7.8

3.3. Optical Properties

3.3.1. Absorbance Spectra

The absorbance spectra of TiO_2 with thicknesses of 278.01, 1630.53, and 2579.66 nm are shown in Figure (3). In the area, TiO_2 nano-thin films' absorbance spectra were captured. Simply said, this spectrum shows a large rise in absorbance intensity as film thickness increases, the increase in thin film thickness causes the highest absorption peak to move to a lower wavelength, which shows that the energy band gap widens as film thickness grows. Additionally, the absorbance spectra show that the TiO_2 nano-thin films have a significant amount of UV absorption.

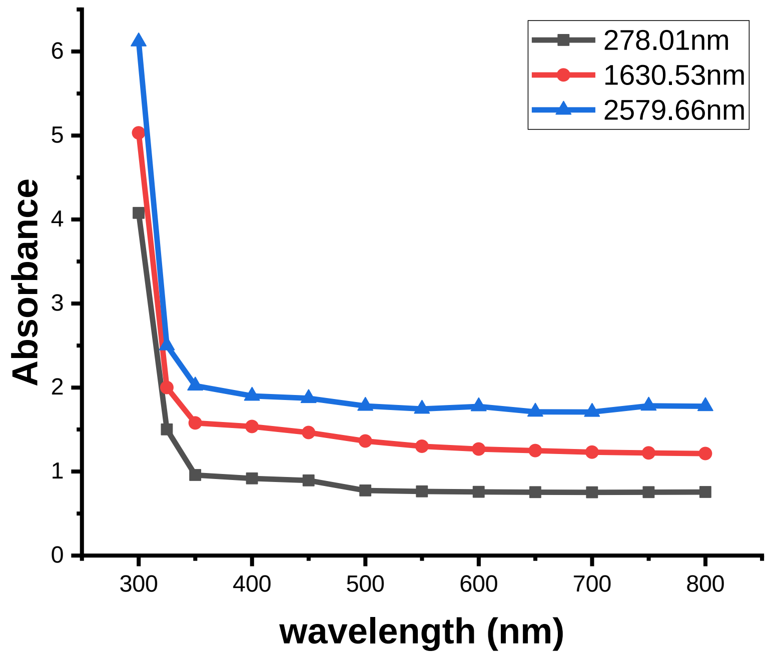

Figure (3). The absorbance spectra of TiO_2 with 278.01, 1630.53, and 2579.66 nm thickness.

3.3.2. Transmittance Spectra

Figure (4) displays the transmittance spectra for TiO_2 with 278.01, 1630.53, and 2579.66 nm thickness. It can be seen that the transmission of these nano thin films is high and encompasses the entire visible spectrum, almost becoming less as the film thickness increases.

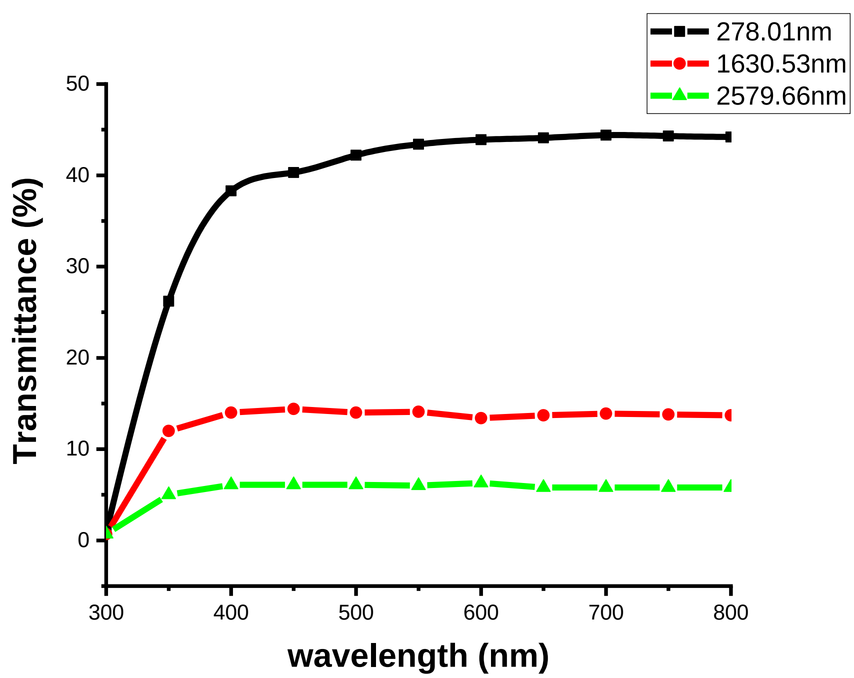

Figure (4). The transmittance spectra of TiO_2 with 278.01, 1630.53, and 2579.66 nm thickness.

3.3.3. Optical Energy Gap

From the knowledge of the absorption coefficient, it was also possible to compute the energy gap of the manufactured films, and it was also possible to determine the type of optical energy gap. If it is more than 104 cm^{-1}, then the energy gap in the samples is of the direct type. This may be deduced from the fact that the value. Establishing a relationship between $(h)^2$ and the energy of the incident photon (h), as shown in Figure (5), was necessary in order to calculate the energy gap of the sample films. This was done by first extending the straight line from the curve until it intersected with the photon energy axis at the point = 0. This made it possible to determine the value of the energy gap, which is shown in Table (5) for the acceptable direct transfers of the pure films. This was made possible because of the fact that this allowed for it. It is important to point out that the value is at Table (5) presents the TiO_2 gap values that correlate laser energy and the thickness of the nano film.

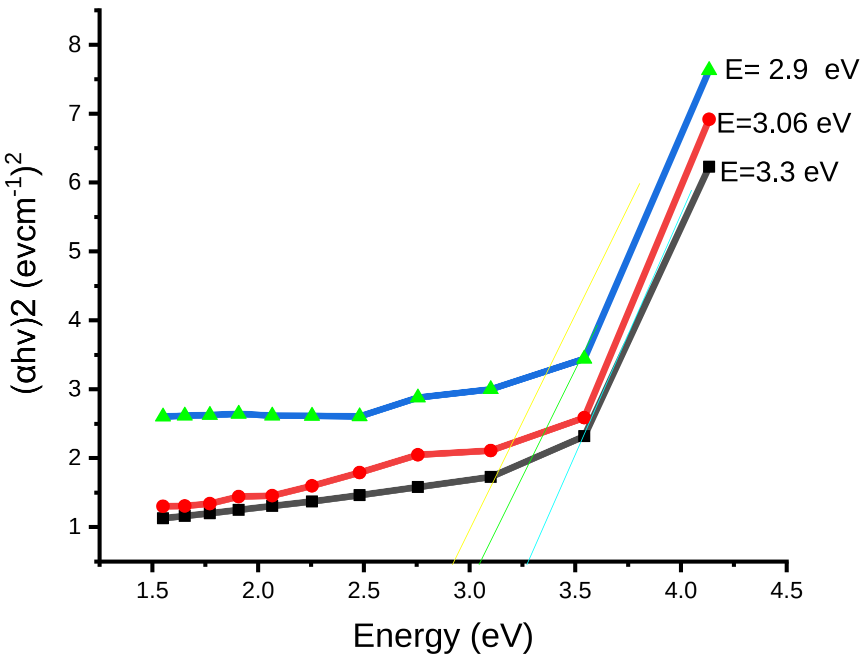

Figure (5). Optical energy gap.

Table (5). Energy gap values corresponding to laser energy and thickness for nano thin film for ZnO and TiO_2.

Sample	Energy gap (eV)
231.01 nm	3.304
1630.53 nm	3.06
2579.66 nm	2.9
TiO_2 nanostructure	(3.2 - 3.29) eV [68].

3.4. Electrical Properties

The investigation of the electrical properties of the cell composed of TiO_2, and Si was performed using an Ossila solar cell measurement, as shown in Table (7). A comparison was made between the results obtained before and after exposure to the annealing process, which was performed at a temperature of 400°C for 2 hours. The noticed a rise in the efficiency of the annealed solar cell compared to the efficiency of the un-annealed cell, and the obtained the highest efficiency for the cell TiO_2 film before annealing (0.07%), after annealing (1.27%). We believe that annealing is responsible for improving the film homogeneity and film density. The best results were at laser energy of 700 mJ.

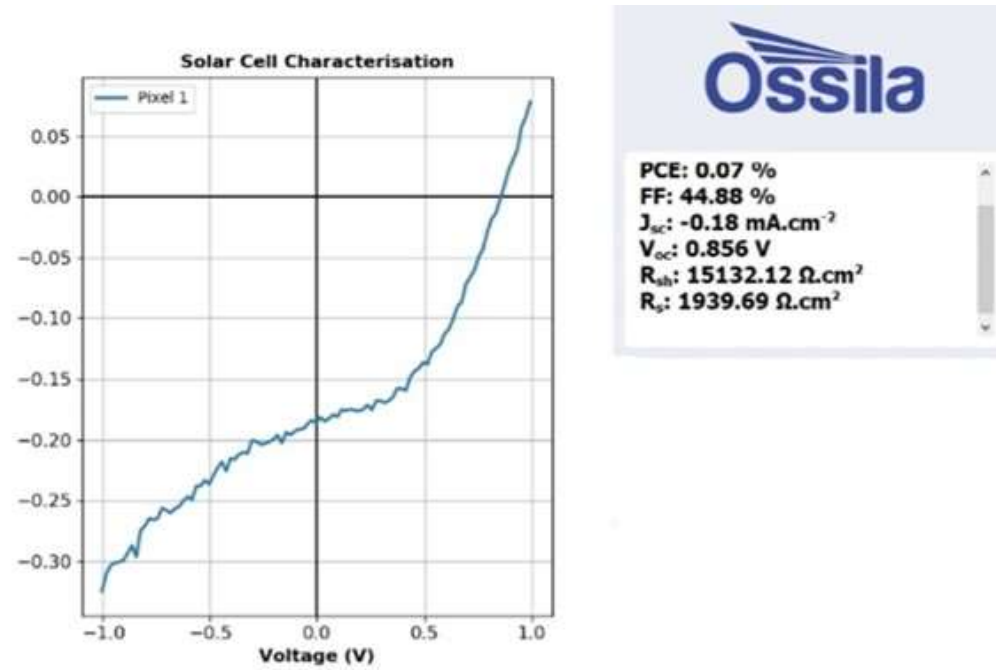

Figure (4). I-J diagram of the silicon solar cell before annealing.

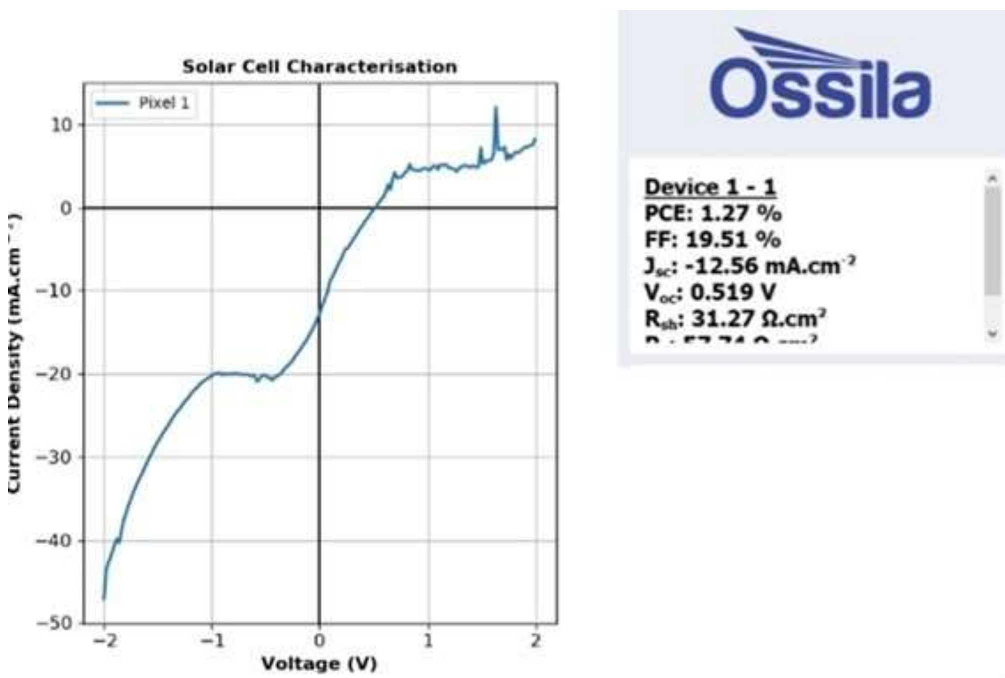

Figure (5). I-J diagram of the Silicon solar Cell after annealing

Table (6). Ossila solar cell measurements.

Experiment Number	PCE (%)	FF (%)	J_{SC} ($mA.cm^2$)	V_{OC} (V)	R_{SH} $\Omega.cm^2$	R_S $\Omega.cm^2$
after annealing	1.27	19.51	-12.56	0.519	31.27	57.70
before annealing	0.07	44.88	-0.18	0.856	15132.12	1939.69

4. Conclusions

The Pulse laser deposition technique is a good method for the synthesis of thin films TiO_2 at different thicknesses, at a constant temperature of 300 ℃, at pulse laser of 250 per minute, with laser energy of 700,800, and 900mJ on a silicon substrate, thin films of n-type TiO_2 were deposited using the pulsed laser deposition process. By using this method, high purity oxides can be produced from high purity powder in new and innovative ways. The results show that TiO_2 thin films enhanced the efficiency of the (p-n) junction solar cell. The following values 1.27% after annealing and 0.07% before annealing. The optical energy direct band gap values in TiO_2 increase with increasing nan thin film thickness and decreasing grain size due to the quantum confinement effect, and these results are consistent with other experimental and theoretical work. TiO_2 also exhibits high UV absorption and high transmittance with a blue shift of the absorption peak.

Conflict of Interest: The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.

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