Enhanced photo-response of porous silicon photo-detectors by embedding Titanium-dioxide nano-particles

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Abstract: Porous silicon (n-PS) films can be prepared by photoelectrochemical etching (PECE) Silicon chips n - types with 15 (mA /cm²), in 15 minutes etching time on the fabrication nano-sized pore arrangement. By using X-ray diffraction measurement and atomic power microscopy characteristics (AFM), PS was investigated. It was also evaluated the crystallities size from (XRD) for the PS nanoscale. The atomic force microscopy confirmed the nano-metric size chemical fictionalization through the electrochemical etching that was shown on the PS surface chemical composition. The atomic power microscopy checks showed the roughness of the silicon surface. It is also notified (TiO₂) preparation nano-particles that were prepared by pulse laser eradication in ethanol (PLAL) technique through irradiation with a Nd:YAG laser pulses TiO₂ target that is sunk in methanol using 400 mJ of laser energy. It has been studied the structural, optical and morphological of TiO₂NPs. It has been detected that through XRD measurement, (TiO₂) NPs have a Tetragonal crystal structure. While with AFM measurements, it has been realized that the synthesized TiO₂ particles are spherical with an average particle size in the (82 nm) range. It has been determined that the energy band gap of TiO₂ NPs from optical properties and set to be in (5eV) range. The transmittance and reflectance spectra have determined the TiO₂ NPs optical constants. It was reported the effectiveness of TiO₂ NPs expansion on the PS Photodetector properties which exposes the benefits in (Al/PS/Si/Al). The built-in tension values depend on the etching time current density and laser flounce. Al/TiO₂/PS/Si/Al photo-detector heterojunction have two response peaks that are situated at 350 nm and (700 - 800nm) with max sensitivity ≈ 0.7 A/W. The maximum given detectivity is 9.38at ≈ 780 nm wavelength.

Keyword: Titanium oxide, XRD, AFM, thin film, photodetector, porous silicon.

1.Introduction
Titanium dioxide is a non-toxic, so metal oxide like TiO₂ thin film have been a general lesson for different applications such as solar cells, photodetector, protective coating and gas sensors [1, 2]. Pulsed laser ablation in ethanol (PLAL) has been employed to output large size of nanomaterials, which have shown a
variety of chemical, optical, magnetic, and electronic properties[3]. For fellow ship, student have centralize on the synthesis of variety materials using this technique in gas phases and liquid with solid [4-5]. Differential number for the every of nanostructures using PLAL, which depend on the precursor materials, the laser parameters and the surrounding conditions, TiO2 is a very suitable oxide material for solar cell and photodetector applications, because of its extraordinary depress ability of photogenerated holes. Thin films are prepared by different preparing methods, TiO2 is considered as one of the most important semiconductors having high photo-catalytic activity, non-toxicity and premium chemical immutability at different stipulation [6]. Thin films can be deposited using several techniques such as, pulse laser ablation ,chemical vapor deposition (CVD) [7] ,spray pyrolysis [8], magnetron sputtering [9] & sol-gel [10] technique. In these methods, sol-gel methods have been notable beneficial, including thin film microstructure uniformity and low at every temperature and cost. Homogeneous layers on different substrates at low cost and it depend on the choice of refractive index and thickness of the layer by changing verbosity stipulation. Thin film crystalline size supposes for were allowed by, X-ray Diffraction (XRD) and using atomic force microscopy(AFM).

2. Experimental
The thin film silicon wafer n-type (100) with resistivity of (2-20) Ω . cm range. The silicon wafer was chemically cleaned . The substrates divided into oblong with (1.5×1.5 cm) areas and 0.1 μm thickness. All layers were precipitated through an evaporation system on the wafer. Photoelectrochemical etching PECE (executes in a mixture of (1:1) / (40%) HF – Ethanol at room temperature using (Au) electrode as 15 mA/cm2 Current densities that was applied for 15 minutes etching time and the etched sample area was(0.785 cm2) as in ‘figure 1’.

![Figure 1](image-url)

Figure 1. a) The schematic diagram of PEC system and b) The photographic image of PEC system.

‘Figure 1’ shows 1 and 3D AFM images of n-PS c synthesized with 15mA/cm2 current density and 15 minutes etching time. It has columnar grains and their average grain size is in the range of 82 nm. The average roughness is (2.43 nm), the AFM image of the irradiated surface exhibits coarser grind and rough surface. The RMS 2.86 nm. The 3D AFM image shows nearly uniform porous surface with valleys and hills and few grains have size larger than the others.
Titanium dioxide nano-particles were created using TiO2 laser ablation under the bullet of (1 cm²) diameter in methanol at room heat. The colloidal sol. Were influenced by the TiO2 pellet brilliance with Nd:YAG laser pulses that were run at λ = 1064 nm. The target was TiO2 which was set up in the filled quartz bottom (5 ml) of solution. Above the target, it was synthesized colloidal solutions by using irradiated pellet of (TiO2) with Nd:YAG laser pulses at λ= 1064 nm (HUAFEI type), It was fixed the laser fluence usage for ablation at 1.32 J/cm² and at five minutes as in 'figure 3'.

Figure 3. Methanol and Colloidal suspensions of TiO2 at 1.32 J/cm² pulse laser fluence from left to right.

TiO2 thin films were deposited on glass and n-Si substrates by by drop (5 drops) casting method, then the samples were annealed at 100°C for 1 hour. XRD-6000 was used to study the deposited films crystalline and structure. Transmission electron microscope (TEM) and (AFM) scanning probe microscope was used to study the film morphology and by utilizing UV–VIS double beam spectrophotometer, thin films absorption was measured.

3. Results and Discussion

3.1 Structure and optical investigation of TiO2 nanoparticles morphology:

XRD analysis is managed to determine the phases and the grain size. XRD types for the investigated TiO2 sample prepared by laser ablation in ethanol and deposited on a glass substrate by the drop casting method. The XRD patterns for samples, show only nine peaks at 25.34, 37.91, 48.16, 54, 55.18, 62, 79, 70.39 and
75.15 corresponding to (101), (004), (200), (105), (211), (213), (216), (120) and (215) planes respectively. These results in agreement with the standard TiO₂ XRD [X-ray diffraction data file [00-021-1272]. It was accounted the crystallite size (D) by using the Scherrer’s formulation. \( D = \frac{0.94 \lambda}{\beta \cos \theta} \) [10], where \( \lambda \) (1.54056 Å) is the X-ray wavelength, \( \theta \) is the Bragg’s angle and \( \beta \) is the full width at half maximum (FWHM) of the diffraction peak in radians. The calculated value of D is presented in (table 1). It can be seen from the values of D that the as-grown TiO₂ layer presents a monocrystalline structure. The macrostrain (\( \varepsilon \))= \( \beta \cos(\theta)/4 \) and dislocation density (\( \delta \))=1/D² have been calculated [11] and their results are demonstrated in (table 1) : micro-strain and dislocation density where \( w \) = the FWHM and \( D \) = the crystallite size.

**Figure 4.** XRD pattern of TiO₂ films nanoparticles

**Table 1.** X-ray Diffraction appointment TiO₂

| 2 Theta (deg) | \( \beta \) (deg) | (hkl) planes | D (nm) | \( \eta \times 10^{-5} \) lines².m⁻¹ | \( \delta \times 10^{14} \) (lines.m²) |
|---------------|-------------------|--------------|--------|-----------------------------------|-----------------------------------|
| 25.4377       | 0.2308            | (101)        | 35.09983 | 9.871841                          | 8.116894                          |
| 37.9183       | 0.212             | (004)        | 39.42599 | 8.78862                           | 6.433316                          |
| 48.1607       | 0.2232            | (200)        | 38.80699 | 8.928804                          | 6.640184                          |
| 54.0053       | 0.2068            | (105)        | 42.92989 | 8.0713                            | 5.426009                          |
| 55.1802       | 0.2252            | (211)        | 39.63381 | 8.742536                          | 6.366026                          |
| 62.7984       | 0.230             | (213)        | 40.31191 | 8.595474                          | 6.153655                          |
| 68.8576       | 0.208             | (116)        | 46.14684 | 7.50864                           | 4.69587                          |
| 70.3934       | 0.2087            | (220)        | 46.42786 | 7.463191                          | 4.639195                          |
| 75.1598       | 0.2114            | (215)        | 47.27955 | 7.32852                           | 4.473561                          |

*Figure 5* demonstrates the spectrum transition on TiO₂NPS, this transmittance reaches the maximum value 50% at the UV wavelength (280 nm) then reduces at (380 nm) and increase slowly over that, this is the feature of high nanoparticles transmittance at these wavelengths thus, the transmission increased as wavelength increased [12].
The TiO$_2$ energy gaps of nanoparticles were evaluated by using Tauc relation:

$$ahv = (hv - Eg)^{\frac{1}{2}}$$  \hspace{1cm} (1)

Where $E_g$ is the band gap energy, $a$ is the absorption coefficient, $A$ is constant $hv$ is the photon energy.

Figure 5 displays TiO$_2$ band gap that was measured from the square plot of $(ahv)^2$ against photon energy $hv$ (where $a$ = the absorption coefficient) by extrapolating the curve linear part toward the photon energy axis can be found to become (5eV and 5.7 eV). The two energy gap may refer to the absorption edge flux which is because of the energy band structure and the difference of state density with the energy level, this variation can also be assign to the low film thickness.

Figure 7 shows I–V features of Al/TiO$_2$ nano-particles layer contact prepared with 1.32J/cm$^2$ without any post heat at the dark room temperature. It obviously displays an ohmic contact over the whole utilized voltage range. Hall effect measurements which were carried out for TiO$_2$ at room temperature, these measurements assured the n-type conductivity of the collected TiO$_2$ nanoparticles. This is attributed to the
decreasing of titanium to the oxygen rate due to the increasing of Hall mobility. This result is in agreement with AFM and XRD results and because of the structural deficiency reducing.

![Graph showing I-V characteristics](image)

**Figure 7.** Room temperature I–V characteristics of Al/TiO2 nano-particles contact

The TEM image and particle size distributions of TiO2 NPS prepared by laser fluency are shown in ‘figure 8’ The TEM images show that the TiO2 NPs are well crystallized and are mostly separated. The images confirm that the particles have a spherical shape and the particle size was in the range of (44-68 nm). The production of different sizes particles at fixed laser fluency can be explained on the basis that the newly formed nanoparticles, which lie in the direction of laser radiation will have smaller sizes due to their successive interaction with laser pulses by the interpulse absorption process [13].

![TEM images of TiO2 nanoparticles](image)

**Figure 8.** TEM images of TiO2 nanoparticles

Al/TiO2/n-Si/Al heterojunction photodetector was fabricated by using Al metal as an ohmic contacts. The capacity measuring is considered as a function of inverse voltage (C-V) to Al/TiO2/n-Si/Al structure that were done by using (LCZ) meter at (10 kHz). Width of the depletion layer and charge-carrier density ($N_d$) for the two devices are studied by using the ‘as in equation (2)’[14].
\[ W = \sqrt{\frac{2\varepsilon_{\psi}}{qN_d}} V_{bi} \]  
\[ N_d = \frac{2}{q\varepsilon_{\psi}} \frac{dV}{\varepsilon^2 \cdot dc} \]  

\((\varepsilon_{\psi})\) is the dielectric constant, \(dV/dc\) is the tendency revers. For current–voltage measurements, a (UNI-T-UT33C digital electrometer, Tektronics CDM 250 multimeters and double Farnel LT30/2, from (0 - 10V) were utilized. Spectral responsivity measurement was performed using a monochromator (Joban-Yvon monochromator) running at (200-900) nm wavelength range, while the current measurement was achieved by using a 8010 DMM Fluke digital millimeter. Capacitance-voltage characteristics of Al/TiO\(_2\)/PS/n-Si/Al is shown in Figure 9 under different reverse ranging (0-6)V. This figure shows that the capacitance decrease with increasing the supplied reverse voltage, it is noticed that the capacity decreases (non-linear) with increasing the reverse alignment voltage ‘as in equation (2)’. This attitude refers to the depletion region width increasing, this in turn leads to decrease the capacity at the junction sides.

![Figure 9. (C-V) Characteristics plot for Al/TiO\(_2\)/PS/n-Si/Al Hetrojunction](image)

Capacitance- Voltage properties can be employed to estimate and calculate, heterojunction most important Parameters, such as built-in – voltage \((V_{bi})\), depletion region, Carrier concentration, which clear idea concerning. The charge distribution, though out the lager C-V characteristics.

Shown in 'Figure 10 'which represents a linear relation the inverse of the square of capacitance \((1/C^2)\) versus the reverse bias voltage for Al/TiO\(_2\)/PS/n-Si/Al a linear relation is observed in both cases. Also, it can be noticed from the figure Al/TiO\(_2\)/PS/n-Si/Al Will be affected by the application of reverse bias , that the depletion region seems to be extended , inversely it will be getting smaller thickness when forward bias will be applied . The depletion can be treated as a capacitor, with capacitance, C.
Figure 10. $1/C^2$ versus reverse voltage of Al/TiO$_2$/PS/n-Si/Al Heterojunction

Figure 11 shows the I-V dark features in both directions (forward and reverse) of Al/TiO$_2$/PS/n-Si/Al photo-detector that is designed with 15 mA/cm$^2$ current density and constant etching time of 12 minutes. The forward current of all photo-detector is very poor at voltages less than 0.6 V. This current known as reassembly current that takes place at low voltages only. It is created when each electron is excited from valence band in order to obtain the balance back. The second zone at high voltage demonstrates the spreading or bending area, which depends on crowded resistance. In this zone, the chafe voltage is able to deliver electrons with sufficient energy for penetrating the barrier between the two cross sides.

Figure 11. I-V characteristic under forward reverse bias of the Al/TiO$_2$/PS/n-Si/Al

The best features for photodetector heterojunction are the optoelectronic ones, as the incident light power converts to photocurrent can be determined by these features. It can see in figure 12 the invert current-voltage features of the device Al/TiO$_2$/PS/Si/Al that are measured in dark and under diverse light intensity glow, the photo-current under (40 W/m$^2$) Tungsten lamp lighting. It can be noticed that the inverse current
value at a given voltage for Al/TiO2/PS/Si/Al heterojunction under illumination can be higher comparing with in the dark.

![Graph](image-url)

**Figure 12.** Dark and illuminated (I-V) characteristic of Al/TiO2/PS/n-Si/AL Photodetector.

It is inspected the spectral structures responsive through the wavelength range of (200–900) nm with 4V bias, as in equation (4) [15]:

\[
R_x = \frac{I_{ph}}{P_{in}} \text{(A/W)}
\]

As \(I_{ph}\) = the photo-current and \(P_{in}\) = the input power.

The structure of TiO2/PS/n-Si consists of two heterojunction, the first heterojunction is between the TiO2 layer and porous siliconTiO2/PS and the second heterojunction is made between the porous silicon layer and crystalline Silicon (PS/Si). Thus TiO2/PS/n-Si have two depletion regions.

Figures 13 display the spectral responsive plots as a wavelength function TiO2/PS/n-Si structure prepared at etching time 15 min and 15 mA/cm² current density. In figure 11 it can see the spectral response curve of TiO2/PS/n-Si containing two response peaks; the first one is situated at (252 nm) because of the absorption edge of TiO2 nanoparticles, while’s the second one is placed at (780nm) because of the silicon absorption edge.
Figure.13. Responsivity as a function of TiO₂/PS /n-Si photo-detectors wavelength.

Detectivity is reciprocal noise equivalent power of detectors since it depends on the detector area. In order to supply a "Figure of Merit" factor that depends on the actual detector properties, not on how large it occurs. It a term called detectivity that takes the formation [16]:

\[ D_\lambda = \frac{1}{NEP} = \frac{R_\lambda}{I_n} \]  

(\(I_n\)) = noise current and it can occasionally be expressed as:

\[ D_\lambda = \frac{S/N}{P_{in}} \]  

S = the signal, N = the noise and \(P_{in}\) = the input power.

The symbol \(D_\lambda\) represents detectivity and can be stated as D-star that is known (NEP square value)

\[ D_\lambda = R_\lambda \frac{A^{1/2} \Delta f^{1/2}}{I_n} \]  

\[ I_n = \sqrt{2qI_d \Delta f} \]  

\(\Delta f\) = the noise bandwidth. \(D_\lambda\) is independent of the detector area. Therefore the directivity can measure the radical quality of the detector material itself. When a \(D_\lambda\) value for an optical detector is measured, this is generally measured through a system where the incident light is modified or divided at a frequency (f) in order to make an AC signal, which is later enlarged with an extension bandwidth \(\Delta f\). These quantities should be specific. The subordination of \(D_\lambda\) on the wavelength (\(\lambda\)) and the marking \(D_\lambda(\lambda, f, \Delta F)\) can express the frequency where the measurement and the bandwidth are made. So the reference bandwidth is often (1Hz). The \(D_\lambda(\lambda, f, \Delta F)\) units refer to the detector that is proper to detect weak signals in the noise existence [17]. The importance parameters for photodetector are the certain detectivity which perform a low detectable power. Therefore; the detector display is similar with this parameter. In figure (14) it can see the specific detectivity as a function of wavelength for TiO₂/PS /n-Si Photo-detectors at 15 minutes of etching time and 15 mA /cm² current density.
4. Conclusions

By using laser eradication in methanol at 400 mJ laser flunes, TiO2 NPS were in nanosized. The optical characteristic detected that the TiO2 NPS band gap was specified by the quantum size effectiveness. (XRD) measure exposed that the TiO2 NPS was polycrystalline and had only the tetragonal crystal structure.

TiO2NPS deposition onto PS developed the properties, porous photodetectors. The Al/TiO2/PS/Si/Al photo-detector spectral responsivity was found to be (0.7 A/W) at D/780 nm wavelength because of the silicon absorption edge and porous silicon, was about (0.2A/W) at D/200 nm wavelength due to the TiO2 NPS absorption edge. The highest value of the specific detectivity (Dχ) was pointed to be 9.38 X 10^12 W-1 .cm.Hz-1 and situated at (780 nm) wavelength for Al/TiO2/PS/Si/Al photodetector.

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