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RESEARCH ARTICLE

UV Photovoltaic detector based on Bi doped TiO₂ Fabricated by Pulse Laser Deposition

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Abstract

Pure and doped TiO₂ with Bi films are obtained by pulse laser deposition technique at RT under vacume 10⁻³ mbar, and the influence of Bi content on the photovoltaic properties of TiO₂ heterojunctions is studied. All the films display photovoltaic in the near visible region. A broad double peaks are observed around $\lambda = 300\text{nm}$ for pure TiO₂ at RT in the spectral response of the photocurrent, which corresponds approximately to the absorption edge and this peak shift to higher wavelength (600 nm) when Bi content increase by 7% then decrease by 9%. The result is confirmed with the decreasing of the energy gap in optical properties. Also, the increasing is due to an increase in the amount of Bi content, and shifted to 400nm when annealed at 523 K as results of decreasing the energy gap.

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INTRODUCTION

Ultraviolet (UV) photodetector has been a popular research issue for its potential applications in a wide range of fields, such as remote control, chemical analysis, and water purification, flame detection, early missile plume detection, and secure space-to-space communications [1]. Titanium dioxide (TiO₂) has attracted much attention in recent years due to its great potential for applications in optical elements, electrical insulation, capacitors or gates in microelectronic devices, photovoltaic solar cells, antireflection coatings, optical waveguides, photonic crystals [2], devices based on metal etc [3]. Titanium dioxide has been considered to be a photoconductive materials and one of p-type semiconductor materials. It is an n-type semiconductor with a wide band gap (anatase 3.2V), and has been researched in many aspects, such as solar cell [4], photocatalysis [5], sensor and [6]. The wavelength selectivity and distinctive photoelectric properties make TiO₂ are very suitable for UV detection/photo-voltaic conversion [7-9]. Traditionally, there are many ways to integrate the particle or porous TiO₂ layer into nanoelectronic devices. Most of studies are performed on nanogranular films [9]. Titanium Dioxide is extensively used because of its some important properties like high refractive index, non-toxicity and chemical inertness in the presence of acid and basic environment due to these properties it has many potential applications in photocatalysis, polymer industry, white pigment [10] and gas sensor and corrosion protection coating [11]. TiO₂ exists in three phases: rutile, anatase and brookite. Both rutile and anatase have tetragonal crystal structure and brookite has orthorhombic structure. Anatase is a useful catalyst in photochemistry because of its high photoactivity and rutile are common white pigment being employed for its superior optical hiding power, [12].

2. Experimental

2.1 Material

Pure titanium oxide powder and different Bi doping concentrations with high purity (99.999%) pressing it under 5 Ton for five minute to formed a target with 2.5 cm diameter and 0.4 cm thickness. Thin films were prepared by PLD technique using Nd:YAG (Huafei Tongda Technology—DIAMOND-288 pattern EPLS) with $\lambda = 1064$ nm SHG Q-switching laser beam at 700 m_j pulse width 10 ns, repetition frequency (6Hz) for 500 laser pulse is incident on the target surface making an angle of 45° with it.

2.2 PLD TiO₂:Bi thin film preparation:

The pulsed laser deposition experiment is carried out inside a vacuum chamber generally at (10^{-3} Torr) vacuum conditions, at low pressure was used to prepare the films. p-type Si wafer with (111) orientation was rinsed with acetone and methanol to remove dirt. In order to remove the native oxide layer on the samples, they were etched in diluted HF acid (1:10).The substrate is placed in front of the target with its surface parallel to that of the target. Sufficient gap is kept between the target and the substrate so that the substrate holder does not obstruct the incident laser beam. Modification of the deposition technique is done by many investigators from time to time with the aim of obtaining better quality films by this process. These include rotation of the target, heating the substrate, positioning of the substrate with respect to target. The scheme structure of deposited films on Si wafers to prepare TiO₂:Bi /p-Si heterojunctions is shown in Fig.1.

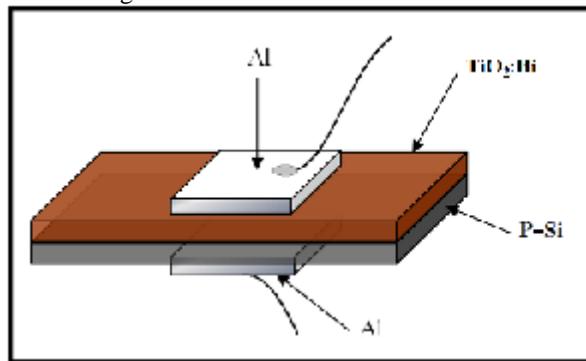


Fig.(1) Schematic device structure of the Al/TiO₂:Bi /Si/Al heterojunction ultraviolet photodetector

2.3. Characterization of Bi doped TiO₂ Thin films

The phase structural characterization of the thin films were determined XRD diffractometer SHIMADZU XRD-6000 X-ray diffractometer with CuK α radiation $\lambda=1.54$ Å as an X-ray source at 40kV and 20mA with 2θ range from 20° to 60. Surface morphology was measured using Atomic Force Microscopy (AFM) (Scanning probe Microscope type AA3000), supplied by Angstrom Advanced Inc. The Photovoltaic properties of TiO₂:Bi thin films were investigated using the testing unit consists of : DC power supply (0-15V , 0-2 A), a variable resistance is used to limit the detector bias current . A PC-interfaced digital Multimeter and Laptop PC are used to register the output circuit current. The UV – Led is used as a UV source for illumination of the TiO₂:Bi photoconductive UV detector. The optical power of the UV Led is 2.5mW and the wavelength is about 385 nm

3. Results and Discussion

Fig. (2) Shows the X-ray diffraction for as deposited TiO₂ films prepared at RT at different concentration of Bi ratio (0, 3, 5, 7 and 9) %. We can observe from this figure that amorphous structure for pure TiO₂ convert to polycrystalline structure contain Anatase and the Rutile TiO₂ phase and the preferred orientation for TiO₂ film doped with (3-7%) Bi ratio appear at 2θ about 27.5° for (110) plane for Rutile phase. This results agreement with the results of researches (13,14,15).Also, it is cleared that the peaks intensities increase with increasing of the doping ratio from 0 to 7% and then decrease for film doped with 9 % Bi. Fig.(3) Shows the X-ray diffraction of annealed TiO₂ films at 523K and with different doping ratio with Bi (0, 3, 5, 7 and 9) %. We can observe that all films have polycrystalline structure contain Anatase and Rutile TiO₂ phase and the preferred orientation for TiO₂ film doped with (3-9%) Bi ratio appear at 2θ about 27.5° for (110) plane for Rutile phase. The peaks intensities increase with increase the doping ratio from 0 to 7% and then decrease at film doped with 9 % Bi and appear some peaks for Bi. In general the grain size increased with increase the Bi content from 0 to 9%.

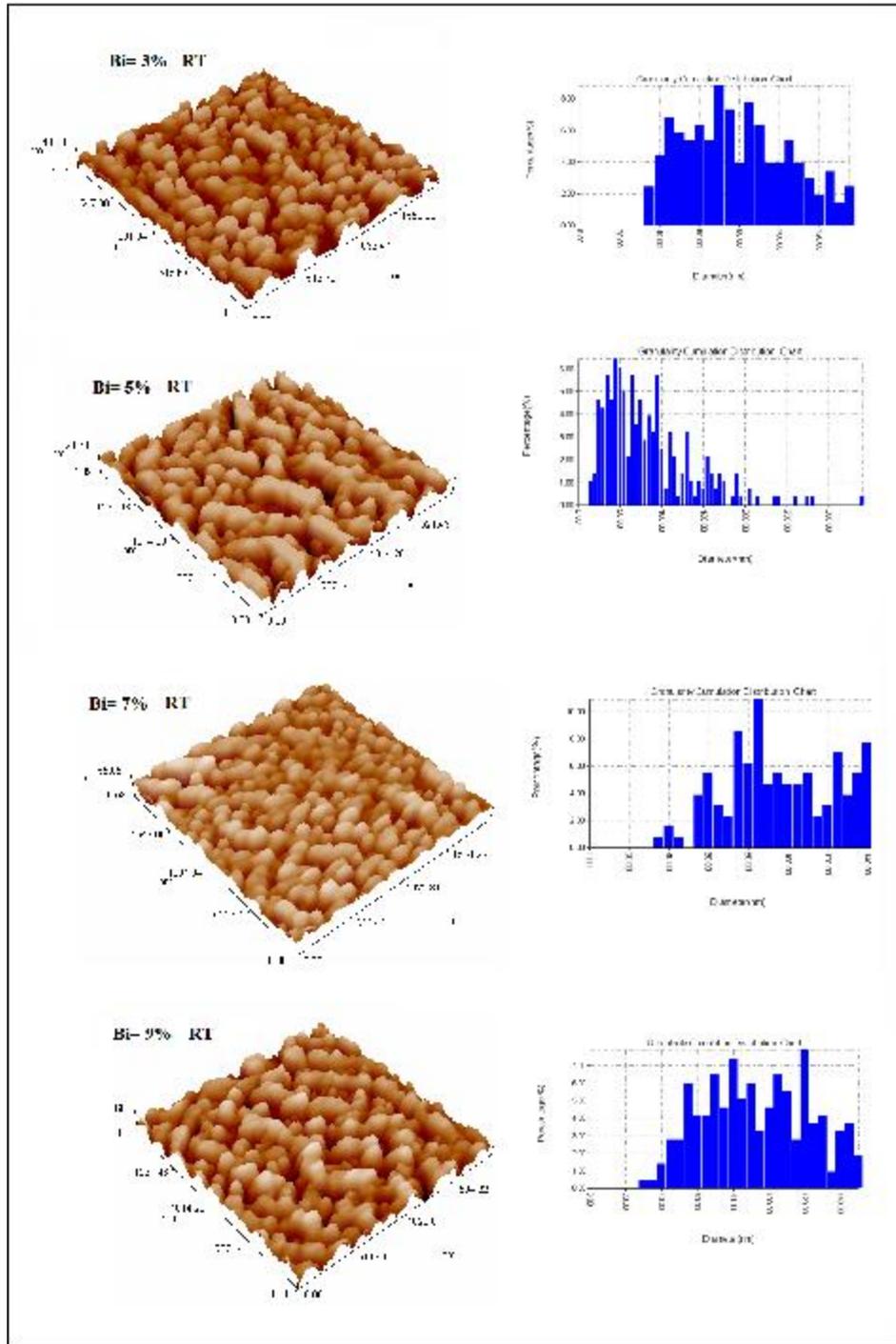


Fig.(4) AFM pictures and their granulometry accumulation distribution for as deposited TiO₂ films with different Bi content ratio (0, 3, 5, 7 and 9) wt%.

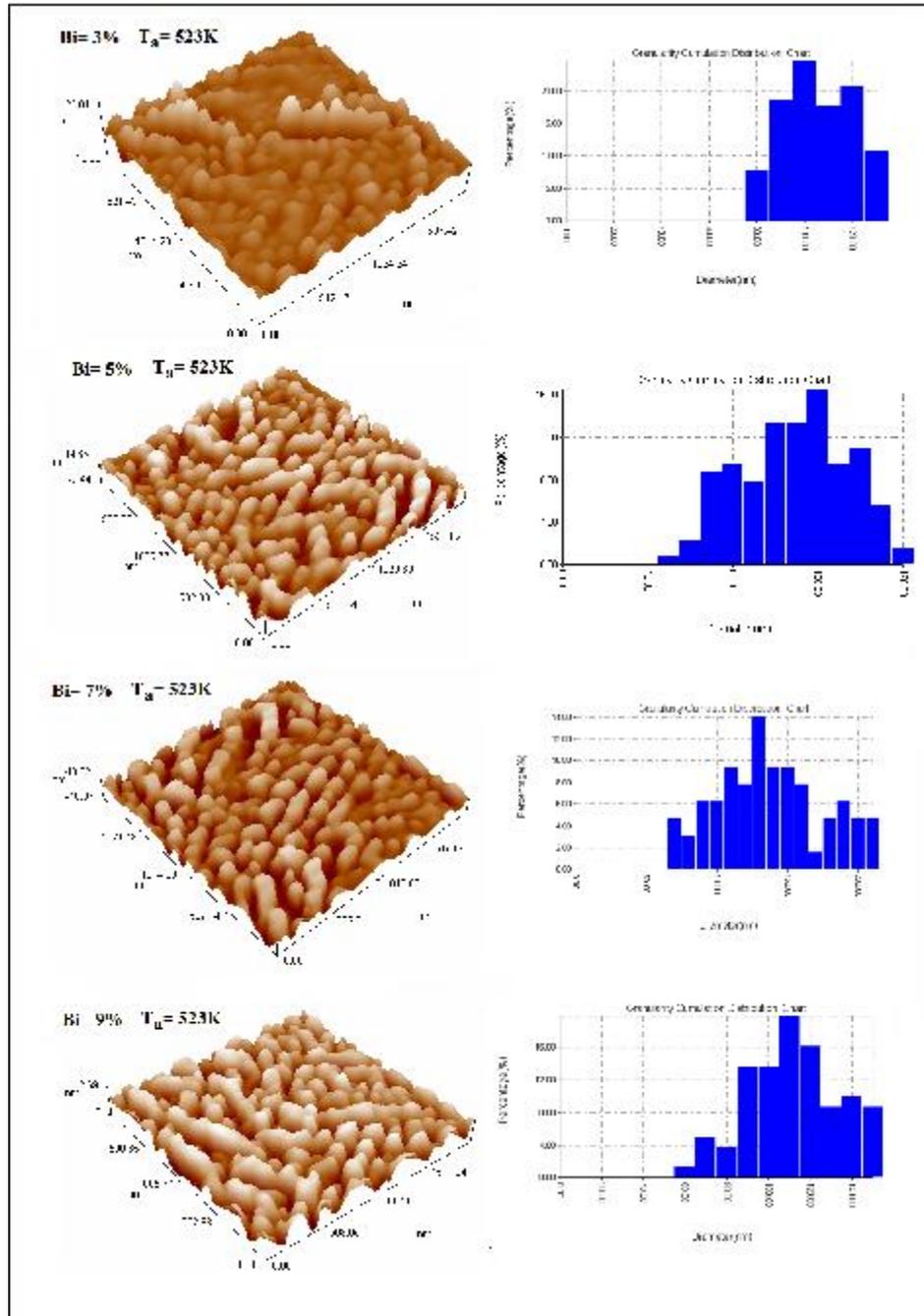


Fig.(5) AFM pictures and their granulometry accumulation distribution annealed to 523K for TiO₂ films with different Bi content ratio (0, 3, 5, 7 and 9) wt%.

Table (1) illustrate an increment in average diameter with increasing doping ratio from 3-7% then decrease at 9% ,while its increase with increasing annealing temperature. This behavior is in agreement XRD results and with the previous work [16]. The films with 7% Bi content, for all annealed temperature, have maximum values of roughness and peak –peak values.

Table (1) AFM parameters for doped TiO₂ films at different Bi content

Ta (K)	Bi%	Average diameter (nm)	Average roughness (nm)	Peak –Peak (nm)
RT	3	76.25	5.31	20.2
	5	81.29	3.32	14.9
	7	95.08	6.89	45.5
	9	90.63	1.74	9.70
523	3	100.62	0.75	10.5
	5	103.40	7.29	39.1
	7	132.21	8.21	44.5
	9	106.85	0.74	3.86

3-1 Spectral Responsivity (R_λ)

Spectral responsivity(R_λ) is the most important parameter by which the range of heterojunction operation can be determined using the equation [17]

$$R_{\lambda} = \frac{I_{ph}}{P_{in}} \text{ or } R_{\lambda} = \frac{V}{P_{in}} \dots\dots\dots(1)$$

The responsivity values of n-TiO₂:Bi/p-Si were calculated from measured photo current for as deposited and annealed films at 523K for pure and doped TiO₂ with different concentration of Bi (0, 3, 5, 7 and 9) % are shown in Fig.(6 and 7) respectively. It is found from this Figure that (R_λ) increases with the increasing of wavelength up to highest responsivity is achieved at near the cut-off wavelength, then it is reduced sharply.

In general, it is found that the film becomes more sensitive and the value of the peak of spectral response increases when the value of x is increased .These figures show that the responsivity increases with increasing of Bi content from 0 to 9% and annealing temperatures. Also, it was observed that the peak at maximum responsivity occurred at λ= 300nm for pure TiO₂ at RT and this peak shift to higher wavelength (600 nm) when Bi content increase to 7% this result is confirmed with the decreasing the energy gap in optical properties also the increasing is due to an increase in the amount of Bi content leading to increase the absorption coefficient and this is because, the forbidden bands TiO₂ decrease when the value of x is increased as we mentioned previously and increases the quantum efficiency and consequently R_λ increases .The spectral responsivity increases with increasing of the annealing temperature due to increasing of the photocurrent and the peak shift to 400 nm at x 0.7% when annealed at 523 K , i.e to higher photon energy also because of the increasing the efficiency to separate the electron-hole pairs by the internal electric field. All the value of responsivity for all the films is tabulated in the table (2). We can see from the same Table that the peaks of R_λ are shifted to shorter wavelength i.e higher photon energy as the annealing temperature increases due to the increase of optical energy gap.

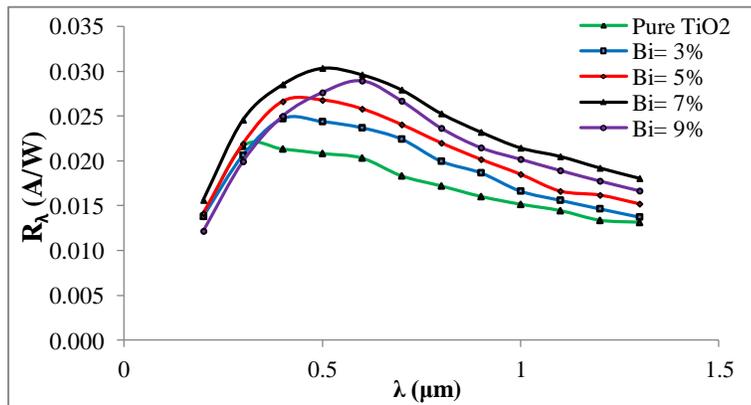
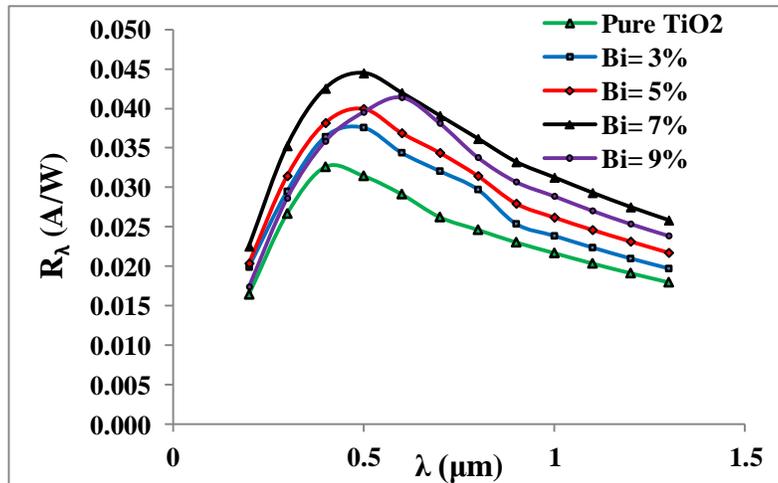


Fig (6) Variation of responsivity with λ for as deposited TiO₂ films at RT at different Bi content (0, 3, 5, 7 and 9) %.



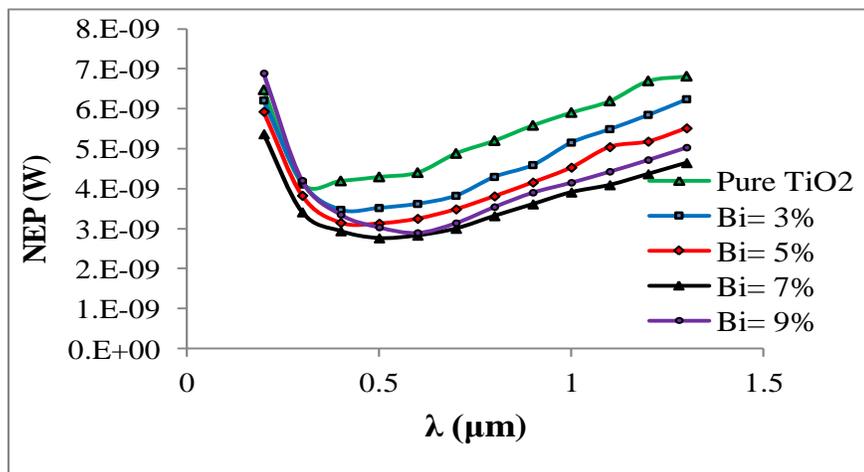
Fig(7) Variation of responsivity with λ for annealed TiO_2 films at 523K at different Bi content (0, 3, 5, 7 and 9) %.

3-2 Noise Equivalent Power (NEP)

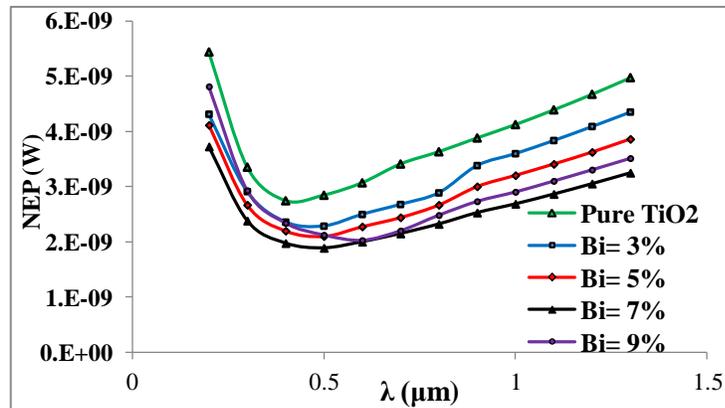
Noise equivalent power (NEP) is defined as the root mean square (r.m.s) incident radiant power falling on the detector that is required to produce an (r.m.s) signal voltage or current equal to the (r.m.s) noise voltage or current at the detector output [18] . It is expressed as:

$$NEP = I_n / R_\lambda \dots\dots\dots 2$$

The noise equivalent power (NEP) values for as deposited and annealed films at 523K, are shown in figure (8 and 9). These figures show that the (NEP) decrease with increase Bi content from 0 to 7% then increase at 9%. and decrease with annealing.



Fig(8) Variation NEP with λ for as deposited TiO_2 /Si detector at RT at different Bi content (0, 3, 5, 7 and 9) %.



Fig(9) Variation NEP with λ for annealed TiO_2/Si detector at 523K at different Bi content (0, 3, 5, 7 and 9) %.

3-3 Specific Detectivity (D^*)

The detectivity (D) is defined as the signal – – noise ratio per unit incident radiation power and it is defined as [18]:

$$D = 1/NEP \dots\dots\dots-3$$

The variation of specific detectivity (D^*) as a function of wavelength for n- $TiO_2:Bi/p-Si$ heterojunction at different x content and annealing temperatures to 523K is presented in as shown in figures (10 and 11).These figures show that the specific detectivity increases with increasing of Bi content from 0 to 7% then decrease at 9%, and increased with annealing temperature. This increasing is due to decrease of NEP as shown previously.

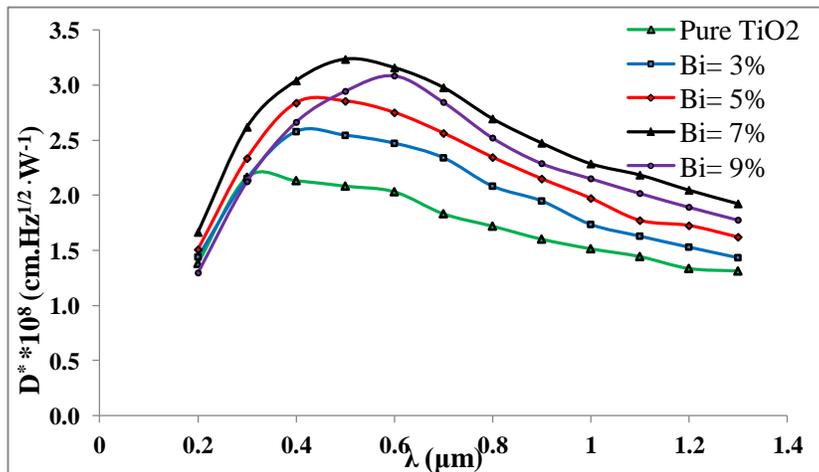
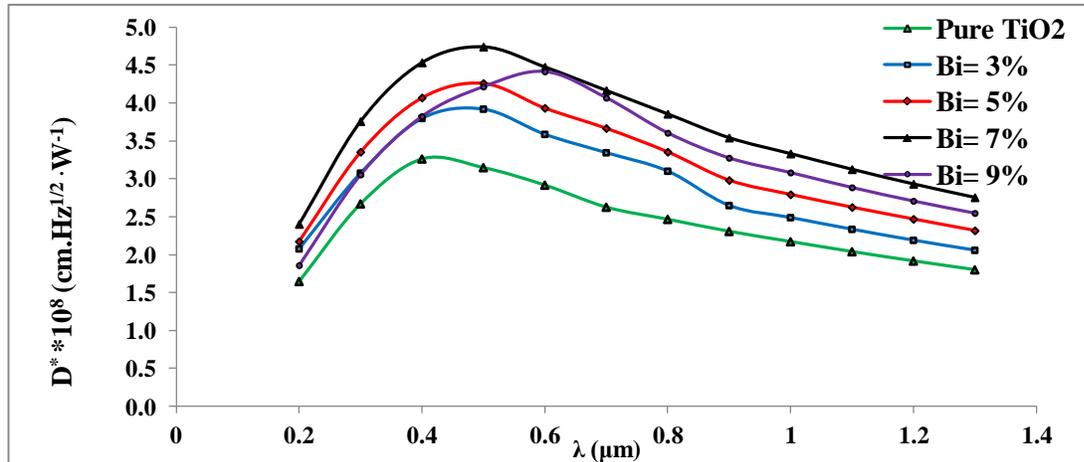


Fig (10) Variation of specific detectivity with λ for as deposited TiO_2/Si detector at RT at different Bi content (0, 3, 5, 7 and 9) %.



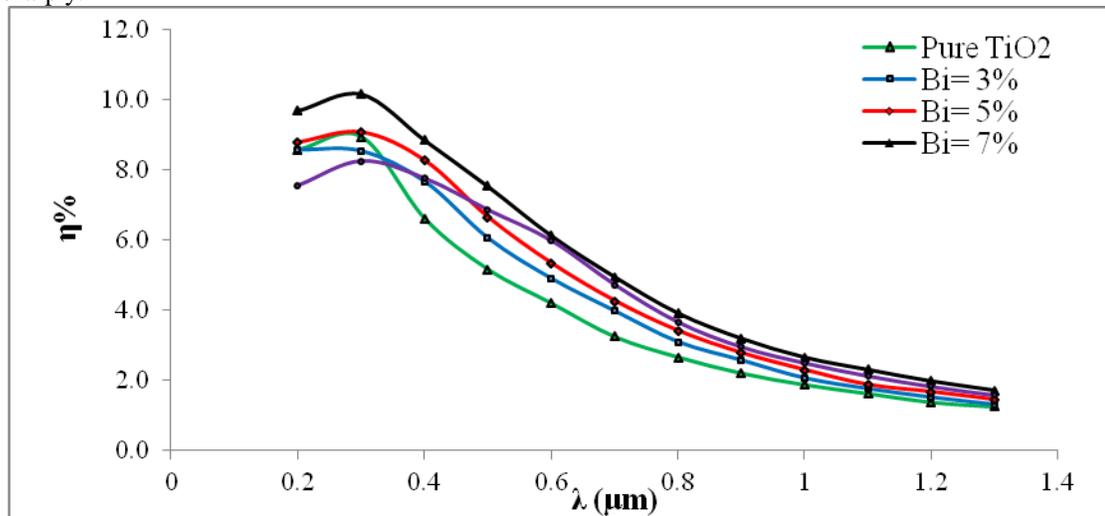
Fig(11) Variation of specific detectivity with λ for annealed TiO_2/Si detector at 523K at different Bi content (0, 3, 5, 7 and 9) %.

3-5-4 Specific efficiency (η)

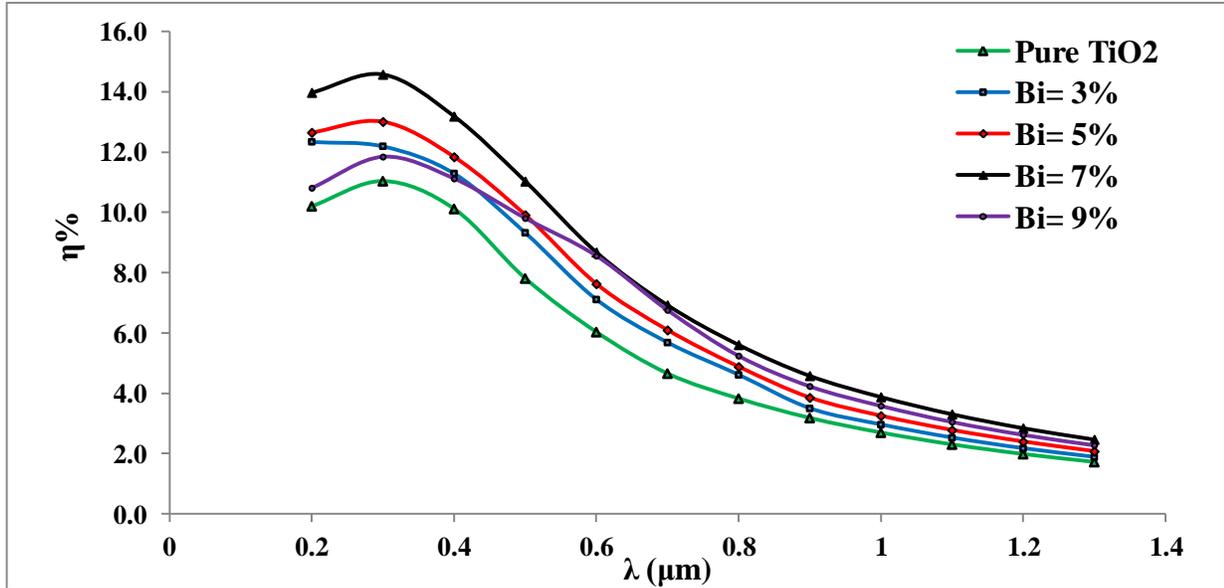
The quantum efficiency (η) represents very important parameter in the photovoltaic devices which is recognized by the optoelectronic effect, which means the ratio between the numbers of generated electrons in the heterojunctions to the number of incident photons on the effective area of the heterojunctions. Is calculated.^[18]

$$\eta = (1-r)(1-e^{-\alpha t})/(1-e^{-\alpha t}) \dots\dots\dots \leq 1 \dots\dots\dots (4)$$

The Specific efficiency (η) values, for as deposited and annealed films at 523K, are shown in figures (12 and 13). These figures show that (η) in general increase with increase Bi content and annealing. Also, from this figure, we can see that D^* increases with increasing wavelength up to the highest detectivity at near the cut off, after that it reduced sharply.



Fig(12) Variation of η with λ for as deposited TiO_2/Si detector at RT at different Bi Content (0, 3, 5, 7 and 9) %.



Fig(13) Variation of η with λ for TiO_2/Si detector annealed at 523K at different Bi content (0, 3, 5, 7 and 9) %.

Table (2) shows the $\text{TiO}_2:\text{Bi}/\text{Si}$ detector parameters (R_λ , λ_m , D^*_{max} , NEP_{min} and η_{max}) for as deposited and annealed films at 523 K at different Bi content (0, 3, 5, 7 and 9) wt %.

Table (2) $\text{TiO}_2:\text{Bi}/\text{Si}$ detector parameters with different Bi doping ratio and annealing temperatures

Ta (K)	Bi (%)	Max(R_λ) (A/W)	λ_m (μm)	Max(D^*)* 10^8 ($\text{cm.Hz}^{1/2} \cdot \text{W}^{-1}$)	Min(NEP)* 10^{-9} (W)	Max(η) (%)
RT	0	0.0216	0.30	2.163	4.135	8.94
	3	0.0247	0.40	2.578	3.469	8.57
	5	0.0268	0.50	2.855	3.132	9.06
	7	0.0304	0.50	3.236	2.764	10.16
	9	0.0290	0.60	3.086	2.898	8.24
523	0	0.0326	0.40	3.261	2.743	11.03
	3	0.0376	0.50	3.919	2.283	12.34
	5	0.0400	0.50	4.260	2.099	13.00
	7	0.0445	0.50	4.741	1.887	14.57
	9	0.0414	0.60	4.414	2.026	11.84

4. Conclusion

In conclusion, TiO_2 a photovoltaic UV detector was developed using different concentration of Bi prepared by pulse laser deposition technique. This device exhibits a prominent performance for UV light detection UV detector demonstrates high photosensitivity and excellent spectral selectivity for all samples. All of these results indicate that this novel UV detector can be a promising candidate as a low-cost UV photodetector for commercially integrated photodetector. The responsivity, quantum efficiency and the specific directivity for $\text{TiO}_2:\text{Bi}/\text{Si}$ detector increase with annealing and with increase Bi content from 0 to 7% then decrease at 9% , while the NEP has inverse behavior. The responsivity reached peak at $\lambda = 300$ nm for pure TiO_2 and this peak shift to 600 nm when Bi content increase to 7% and shifted to 400 nm when annealed at 523 K as a results of decreasing the energy gap

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