# The Influence of Bi content on The Structural and Optical Properties of thin $TiO_{2\,(1-x)}$: Bix Films Prepared by pulse laser deposition

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***Abstract*—**In this study, pure and doped $TiO_2$ with Bi were deposited on glass substrates by pulse laser deposition (PLD) technique at a constant deposition parameter such as : (pulse Nd:YAG laser with λ=1064 nm, constant energy 800 mJ , repetition rate 6 Hz and No. of pulse (500) .These films are annealed to 523K .The structural and optical properties for thin $TiO_{2(1-x)}Bi_x$ films prepared by pulse laser deposition technique have been studied as a function of Bi content. This study shows that the films have polycrystalline structure with good identically and standard peaks for Anatase and Rutile phases. The optical studies reveal that the transition is direct with band gap value from 3.26 eV to 3.14eV with increasing of Bi content from 0 to 9 wt%.

***Keywords*—** TiO2 thin film, pulse laser deposition technique, optical properties, Structural properties

## I. Introduction

Titanium dioxide $TiO_2$ (Titania) is exists in three crystalline structures: rutile, anatase and brookite [1, 2]. The anatase phase is especially adequate for those applications due to its crystal structure and a higher band gap of 3.2 eV compared to the 3 eV in rutile. Anatase and rutile have properties of interest for sensing applications [3]. For calcinations processes above 700 ºC all anatase structure becomes rutile, some authors also found that 500 ºC would be enough for phase transition from anatase to rutile when thermal treatment takes place [4].

Many different techniques such as chemical vapor deposition, electrophoretic deposition (EPD), Spin coating, pulsed laser deposition (PLD), and spray pyrolysis technique have been used to growth the $TiO_2$ [6-8].

Among the various thin film deposition techniques, pulse laser deposition is one of the simplest growth techniques to deposit high quality films and nanostructures under optimized conditions of variety of materials ranging from superconductors to semiconductors to dielectrics to metals and many more [9].

## II. Theoretical Part

XRD is a nondestructive technique for determining lattice parameters, preferred orientation of the crystal, phase composition (qualitatively and quantitatively), grain sizes, lattice strain, residual stress etc. The interplaner distanced dhkl for different planes is measured using Bragg law [10]

$$2d \sin\theta = m\lambda \qquad ..1$$

While the average crystallite size (D) estimated by Scherrer's formula [11]:

$$D = \frac{0.89\,\lambda}{\Delta(2\theta).\cos(\theta)} \qquad .2$$

The semiconductor absorbs photon from the incident beam, the absorption depends on the photon energy (hν); where h is Plank's constant, ν is the incident photon frequency. The absorption coefficient (α) of thin films was calculated from the optical transmittance spectrum measurements using the formula [12]:

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \ldots 3$$

Where t is the thickness of thin films, and T is the transmittance intensity. The energy gap and optical constants were calculated for two samples.The optical energy gap values ($E_g$) for thin $TiO_2$ films on glass have been determined by using Tauc equation [13].

$$\alpha h\upsilon = A\left(h\upsilon - E_g\right)^2 \ldots 4$$

Where hυ is the photon energy, $E_g$ is the optical band gap energy, A is inversely proportional to amorphousity. The energy gap ($E_g$) is then

determined by the extrapolation of the linear portion with hυ axis at $(\alpha h\upsilon)^2 = 0$.It is important to determine the optical constants of thin films such as refractive index (n), extinction coefficient (k), and the real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of dielectric constant.

The extinction coefficient [14]

$k = \alpha\lambda / 4\pi$ ..5

The index of refraction was estimated from the reflectance (R) data using the relation [14].

$$n = \sqrt{\frac{4R}{(1-R)^2} - k^2} - \frac{R+1}{R-1} \quad \ldots.6$$

The real and imaginary parts of dielectric constant were evaluated using the formulas [15]:

$\varepsilon_r = n^2 - k^2$ ……7

$\varepsilon_i = 2nk$ ….8

## III. Experimental Procedure

Pure titanium dioxide powder with high purity (99.99%) and doped with different concentration of Bi (3, 5, 7 and 9) wt% were prepared by pressing less than 5 Ton to formed a target with 2.5 cm diameter and 0.4 cm thickness. It should be as dense and homogenous as possible to ensure a good quality of the deposit. Prior to deposit films, The preparation target of TiO2(1-x):Bix were sintering to temperature of 773K for one hour and then cooled to room temperature. The temperature of the furnace was raised at a rate of 25C0.The glass substrates were cleaned in with cleaner solution, distilled water and followed by alcohol using ultrasonic bath .Thin films of TiO2(1-x):Bix at different Bi contents (3,5,7 and 9 ) % were prepared on glass substrate by (PLD) technique under a vacuum chamber generally at ($10^{-3}$ Torr). Using Nd:YAG laser (Huafei Tongda Technology—DIAMOND-288 pattern EPLS) SHG Q-switching beam (laser Power= 700 MJ, λ = 1064 nm and f=6Hz) coming through a window is incident on the target surface making an angle of 45° with it. 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. The thickness of prepared films was about 500 nm which measured by Michelson interferometer. [16].X-ray diffraction (XRD) pattern of the CdS film deposited on corning glass substrate is recorded by SHIMADZU XRD-6000 X-ray diffractometer (CuKα radiation λ=0.154nm) in 2θ range from 20° to 60°. The absorption spectrum of pure and doped TiO2 films on glass substrate is measured using OPTIMA SP-3000 UV–VIS spectrophotometer covering a range from (200 – 110 nm) by using glass substrate as a reference.

## IV. Results and Discussion

Fig. (1) shows the X-ray diffraction of annealed $TiO_2$:Bi films at 523K and with different doping ratio (Bi=0, 3, 5, 7 and 9) wt%. Table (1) shows the experiment and the standard peaks from International Centre for Diffraction Data (JCPDS) for Anatase $TiO_2$, Rutile $TiO_2$, and Bi crystal,. We can observe that all films have polycrystalline structure contain Anataseand Rutile $TiO_2$ phase and the preferred orientation for $TiO_2$ 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 addition we can also see from table (2) an increasing in $d_{hkl}$ with increasing Bi content i.e., slightly shift in 2θ to lower value because the size of Bi ion (which have been inserted into lattice) larger than for Ti ion

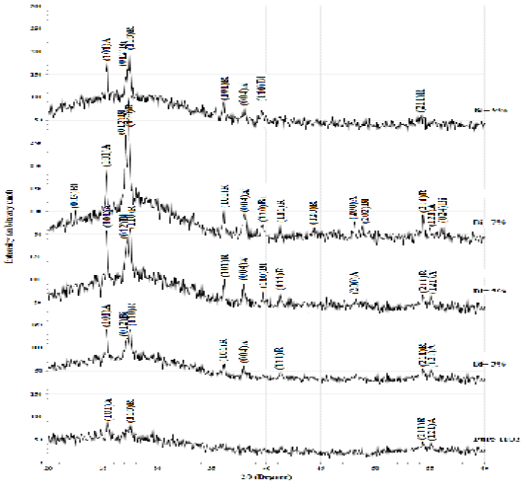

Fig. (1) X-ray diffraction patterns of $TiO_2$:Bi films at different Bi content ( 0, 3, 5, 7 & 9) wt%.

Table (2) Structural parameters: Inter-planar spacing, crystalline

size of annealed $TiO_2$:Bi films at 523K with different Bi content ( 0, 3, 5, 7 and 9) %.

| Bi% | 2θ (Deg.) | FWHM (Deg.) | $d_{hkl}$Exp .(Å) | G.S (D) (nm) | $d_{hkl}$ Std. (Å) | hkl | phase | card No. |
|---|---|---|---|---|---|---|---|---|
| 0 | 25.3820 | 0.4061 | 3.5063 | 20.0 | 3.5163 | (101) | Anatase $TiO_2$ | 96-900-8214 |
| | 27.5127 | 0.5076 | 3.2394 | 16.1 | 3.2477 | (110) | Rutile $TiO_2$ | 96-900-4142 |
| | 54.3147 | 0.3553 | 1.6876 | 25.1 | 1.6874 | (211) | Rutile $TiO_2$ | 96-900-4142 |
| | 55.0761 | 0.2538 | 1.6661 | 35.3 | 1.6662 | (121) | Anatase $TiO_2$ | 96-900-8214 |
| 3 | 25.3807 | 0.2538 | 3.5064 | 32.1 | 3.5163 | (101) | Anatase $TiO_2$ | 96-900-8214 |
| | 27.2081 | 0.2538 | 3.2749 | 32.2 | 3.2705 | (012) | Hex. Bi | 96-500-0216 |
| | 27.5127 | 0.2030 | 3.2394 | 40.3 | 3.2477 | (110) | Rutile $TiO_2$ | 96-900-4142 |
| | 36.1421 | 0.3046 | 2.4833 | 27.4 | 2.4875 | (101) | Rutile $TiO_2$ | 96-900-4142 |
| | 37.9695 | 0.2538 | 2.3678 | 33.1 | 2.3786 | (004) | Anatase $TiO_2$ | 96-900-8214 |
| | 41.2690 | 0.3046 | 2.1858 | 27.9 | 2.1873 | (111) | Rutile $TiO_2$ | 96-900-4142 |
| | 54.3147 | 0.5076 | 1.6876 | 17.6 | 1.6874 | (211) | Rutile $TiO_2$ | 96-900-4142 |
| | 55.0761 | 0.2030 | 1.6661 | 44.1 | 1.6662 | (121) | Anatase $TiO_2$ | 96-900-8214 |
| 5 | 25.3800 | 0.2430 | 3.5065 | 33.5 | 3.5163 | (101) | Anatase $TiO_2$ | 96-900-8214 |
| | 27.2081 | 0.2538 | 3.2749 | 32.2 | 3.2705 | (012) | Hex. Bi | 96-500-0216 |
| | 27.4619 | 0.2030 | 3.2452 | 40.3 | 3.2477 | (110) | Rutile $TiO_2$ | 96-900-4142 |
| | 36.1421 | 0.3046 | 2.4833 | 27.4 | 2.4875 | (101) | Rutile $TiO_2$ | 96-900-4142 |
| | 37.9695 | 0.2538 | 2.3678 | 33.1 | 2.3786 | (004) | Anatase $TiO_2$ | 96-900-8214 |
| | 39.7462 | 0.4569 | 2.2660 | 18.5 | 2.2675 | (110) | Hex. Bi | 96-500-0216 |
| | 41.2183 | 0.4569 | 2.1884 | 18.6 | 2.1873 | (111) | Rutile $TiO_2$ | 96-900-4142 |
| | 48.0203 | 0.3553 | 1.8931 | 24.5 | 1.8921 | (200) | Anatase $TiO_2$ | 96-900-8214 |
| | 54.3147 | 0.4061 | 1.6876 | 22.0 | 1.6874 | (211) | Rutile $TiO_2$ | 96-900-4142 |
| | 55.0761 | 0.2030 | 1.6661 | 44.1 | 1.6662 | (121) | Anatase $TiO_2$ | 96-900-8214 |
| 7 | 22.4873 | 0.2030 | 3.9506 | 39.9 | 3.9380 | (003) | Hex. Bi | 96-500-0216 |
| | 25.3299 | 0.2030 | 3.5133 | 40.1 | 3.5163 | (101) | Anatase $TiO_2$ | 96-900-8214 |
| | 27.1066 | 0.1523 | 3.2870 | 53.7 | 3.2705 | (012) | Hex. Bi | 96-500-0216 |
| | 27.3096 | 0.3553 | 3.2630 | 23.0 | 3.2477 | (110) | Rutile $TiO_2$ | 96-900-4142 |
| | 36.0914 | 0.2538 | 2.4866 | 32.9 | 2.4875 | (101) | Rutile $TiO_2$ | 96-900-4142 |
| | 38.0203 | 0.4569 | 2.3648 | 18.4 | 2.3786 | (004) | Anatase $TiO_2$ | 96-900-8214 |
| | 39.6954 | 0.4061 | 2.2688 | 20.8 | 2.2675 | (110) | Hex. Bi | 96-500-0216 |
| | 41.2690 | 0.3046 | 2.1858 | 27.9 | 2.1873 | (111) | Rutile $TiO_2$ | 96-900-4142 |
| | 44.3147 | 0.4061 | 2.0424 | 21.1 | 2.0541 | (120) | Rutile $TiO_2$ | 96-900-4142 |
| | 48.0711 | 0.2538 | 1.8912 | 34.3 | 1.8921 | (200) | Anatase $TiO_2$ | 96-900-8214 |
| | 48.8325 | 0.2538 | 1.8635 | 34.4 | 1.8634 | (202) | Hex. Bi | 96-500-0216 |
| | 54.3655 | 0.1523 | 1.6862 | 58.6 | 1.6874 | (211) | Rutile $TiO_2$ | 96-900-4142 |
| | 55.0254 | 0.1523 | 1.6675 | 58.8 | 1.6662 | (121) | Anatase $TiO_2$ | 96-900-8214 |
| | 56.1929 | 0.3553 | 1.6356 | 25.3 | 1.6353 | (024) | Hex. Bi | 96-500-0216 |
| 9 | 25.3289 | 0.2030 | 3.5135 | 40.1 | 3.5163 | (101) | Anatase $TiO_2$ | 96-900-8214 |
| | 27.1055 | 0.1523 | 3.2871 | 53.7 | 3.2705 | (012) | Hex. Bi | 96-500-0216 |
| | 27.4619 | 0.2030 | 3.2452 | 40.3 | 3.2477 | (110) | Rutile $TiO_2$ | 96-900-4142 |
| | 36.0914 | 0.3046 | 2.4866 | 27.4 | 2.4875 | (101) | Rutile $TiO_2$ | 96-900-4142 |
| | 37.9695 | 0.3046 | 2.3678 | 27.6 | 2.3786 | (004) | Anatase $TiO_2$ | 96-900-8214 |
| | 39.5431 | 0.3553 | 2.2772 | 23.8 | 2.2675 | (110) | Hex. Bi | 96-500-0216 |
| | 54.2640 | 0.5076 | 1.6891 | 17.6 | 1.6874 | (211) | Rutile $TiO_2$ | 96-900-4142 |

Fig. (2) Shows the variation of average grain size versus Bi content. It can being seen an increasing in average grain size with increasing Bi content from 0-7 % then decrease at 9%

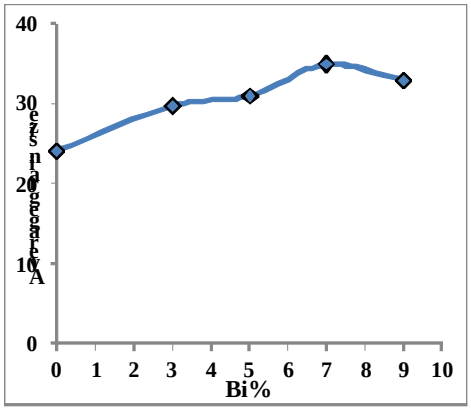


**Fig. (2) average grain size versus Bi content annealed at 523 K**

Figures (3) shows the room temperature transmittance spectra for annealed $TiO_2$:Bi at 523 K with different Bi content . The transmittance at λ =500nm for pure $TiO_2$was found to be 42.2 and decrease with increase the dopant ratio.

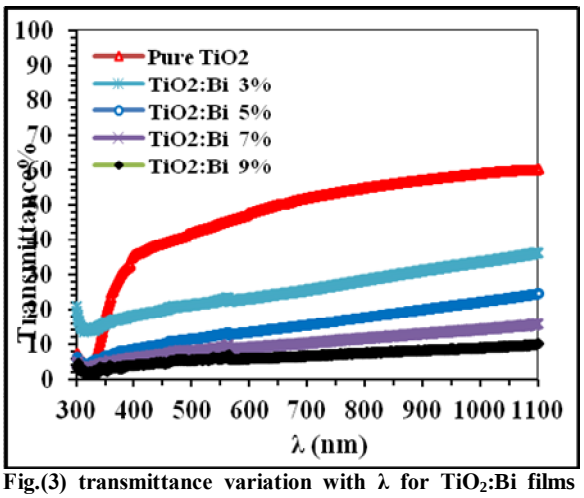


**Fig.(3) transmittance variation with λ for $TiO_2$:Bi films at different Bi content ( 0, 3, 5, 7 & 9) wt%.**

The optical energy gap values ($E_g^{opt}$) for $TiO_2$:Bi films on glass have been determined by Tauc equation. As shown in Figures (4) for different Bi content.

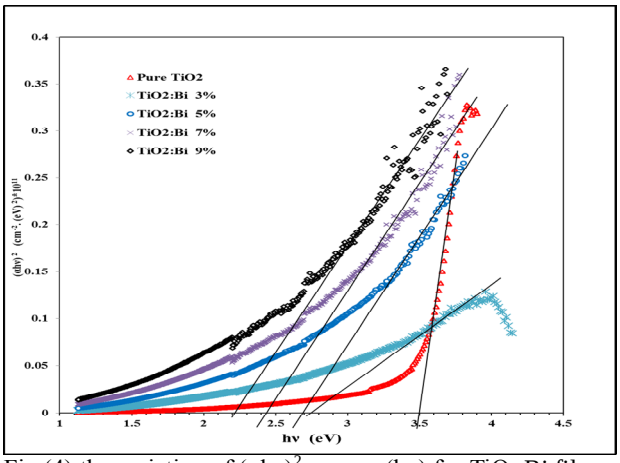


Fig.(4) the variation of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ for $TiO_2$:Bi films at different Bi content ( 0, 3, 5, 7 & 9) wt%.

From the above figures, we can observe that the increasing of Bi content from 0 to 9% leads to decrease the optical band gap from approximately 3.55 eV to 2.25 eV this can be attributed to increase the mineral content, orattributed to increased localized levels of near valence band and conduction band and these levels ready to receive electrons and generate tails in the optical energy gap and tails is working toward reducing the energy gap. This result is consistent with previous researches [17]. Figs.(5) shows the variation of ext6inction coefficient (k) with wavelength at different Bi content and different temperature. We know that the extinction coefficient depends mainly on absorption coefficient; for this reason it has the same behaviour.

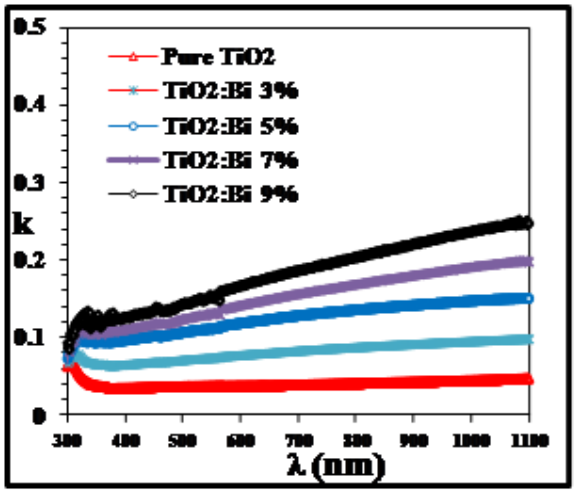


**Fig. (5) variation of extinction coefficient with λ for $TiO_2$:Bi films at different Bi content ( 0, 3, 5, 7 & 9) wt%.**

The variation of the refractive index versus wavelength in the range 300–1100 nm, for deposited $TiO_2$ films on glass with different Bi doping ratio and different annealing temperature have been shown in Fig (6). We can notice from these figures that the refractive index in general decreases with increasing of doping ratio and this behaviour is due to the decrement in energy gap.

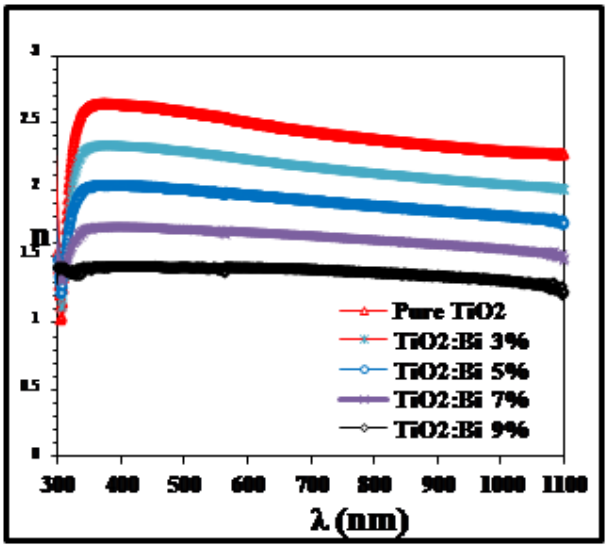


**Fig. (6) The variation of refractive index with λ for $TiO_2$:Bi films at different Bi content ( 0, 3, 5, 7 & 9) wt%.**

The variation of the real and imaginary parts of the dielectric constant values versus wavelength have been shown in figures (7-11 ) for as deposited and annealed $TiO_2$ films at 423K and 523K with different Bi doping ratio ( 0, 3, 5, 7 and 9) %. The variation of the dielectric constant depends on the value of the refractive index. By contrast, the dielectric loss depends mainly on the extinction coefficient values which are related to the variation of absorption.

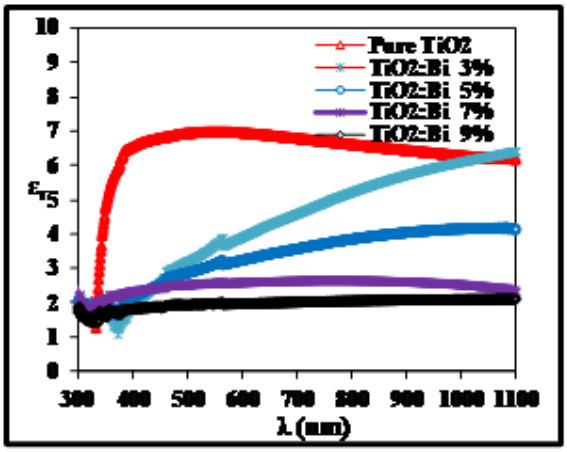


Fig. (7) The variation of $\varepsilon_r$ with the wave length for annealed $TiO_2$ films at 423K at different Bi content ( 0, 3, 5, 7 and 9) wt%.

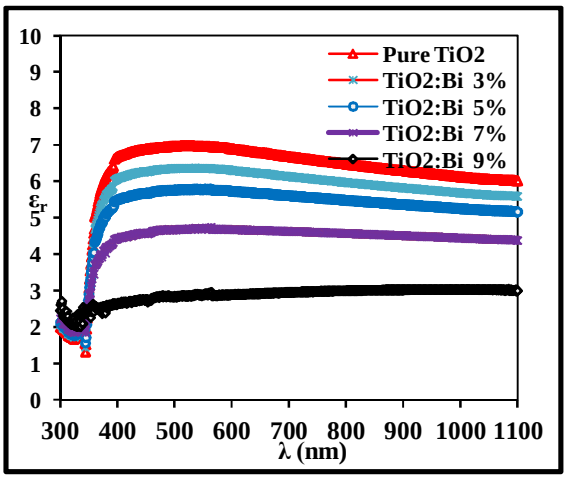


Fig.(8) The variation of $\varepsilon_r$ with the wave length for annealed $TiO_2$ films at 523K at different Bi content ( 0, 3, 5, 7 and 9) wt%.

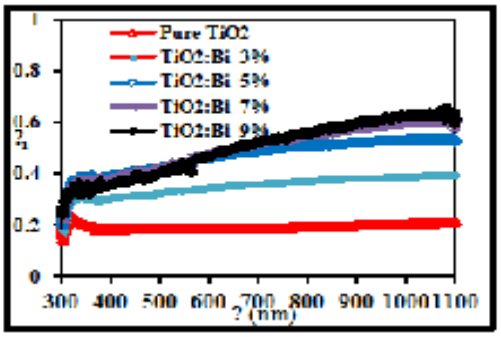


Fig.(9)The variation of $\varepsilon_i$ with the wave length for as deposited $TiO_2$ films at different Bi content ( 0, 3, 5, 7 and 9) wt%

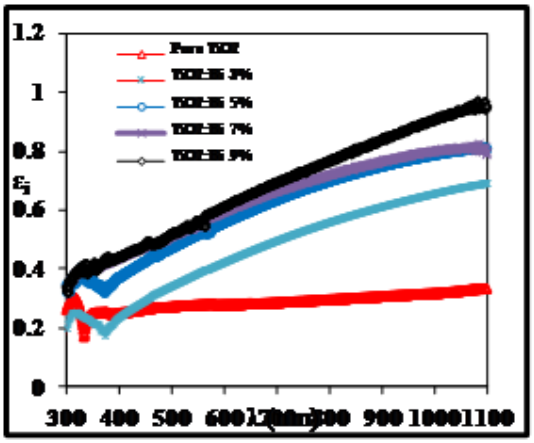


**Fig. (10) The variation of $\varepsilon_i$ with the wave length for annealed $TiO_2$ films at 423K with different Bi content ( 0, 3, 5, 7 and 9) wt%.**

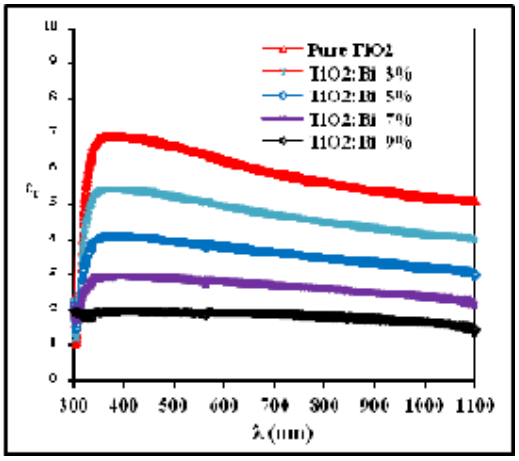


Fig. (11) The variation of $\varepsilon_r$ with the wave length for as deposited $TiO_2$ films at different Bi content ( 0, 3, 5, 7 and 9) wt%.

Table (3) shows the optical constants for pure and doped $TiO_2$ films at Bi deposited by pulses laser on glass substrates with different Bi content (0, 3, 5, 7, 8 and %) and different annealing temperature (RT, 473 and 573) K at λ=500 nm and the energy gap values for these samples.

**Table (3) optical constants for $TiO_2$:Bi films at λ=500 nm and $E_g^{Opt}$ at different Bi content**

| Bi(%) | T(%) | α(cm-1) | k | n | εr | εi | $E_g^{Opt}$ (eV) |
|---|---|---|---|---|---|---|---|
| 0 | 42.21 | 12323 | 0.049 | 2.641 | 6.974 | 0.259 | 3.55 |
| 3 | 21.30 | 22093 | 0.088 | 2.523 | 6.358 | 0.444 | 2.75 |
| 5 | 11.65 | 30714 | 0.122 | 2.405 | 5.769 | 0.588 | 2.70 |
| 7 | 8.14 | 35843 | 0.143 | 2.169 | 4.682 | 0.619 | 2.45 |
| 9 | 5.68 | 40971 | 0.163 | 1.696 | 2.849 | 0.553 | 2.25 |

## V- CONCLUSIONS

Structural and optical properties for anneled $TiO_2$:Bi at 523 K with different Bi contend, prepared by pulse laser deposition technique, have been studied. The outcome of this investigation can be summarized as follows:

- X-ray diffraction pattern for pure and doped titanium dioxide films with different doping ratio with Bi (0, 3, 5, 7 and 9)% show that all films have polycrystalline structure contain Anatase and Rutile $TiO_2$ phase and the preferred orientation for $TiO_2$ 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.
- There is an increasing in $d_{hkl}$ with increasing Bi content i.e., slightly shift in 2θ to lower value because the size of Bi ion.
- Average grain size increase with increasing Bi content from 0-7 % then decrease at 9%.
- The $E_g$ decreases from 3.55 eV to 2.25 eV with increasing Bi content from 0 to 9 wt%.

Increase Bi content leads to decrease (n and $\varepsilon_r$), while (α, k and $\varepsilon_i$) increase with it**.**

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