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Study of Optical and Structures for TiO_2 prepared by Pulse Laser Deposition

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ABSTRACT

Titanium dioxide TiO_2 thin film of 2 μm thickness has been grown on glass substrate by pulsed laser deposition technique at substrate temperature of 500 ^{o}C under the vacuum pressure of 8×10^{-2} mbar. The optical properties concerning the absorption, and transmission spectra were studied for the prepared thin film. From the transmission spectra, the optical gap and linear refractive index of the TiO_2 thin film was determined. The structure of the TiO_2 thin film was tested with X-Ray diffraction and it was formed to be a polycrystalline with many peaks.

Keywords: *TiO_2 thin film, pulse laser deposition*

I. INTRODUCTION

Titanium dioxide (TiO_2) has been proven to be an effective material for application such as photocatlysis [1,2], dye sensitive solar cells [3,4], heterogeneous catalysis [2,5], self-cleaning/antifogging surface coatings [6], etc. Typically, TiO_2 is used in two main form: powder and thin film. The powder form of crystalline TiO_2 is commonly used for gas and liquid phase catalysis. Its photocatalytic activity is normally determined by the particle size [2], phase composition [7], and the position of the conduction and valance bands in the energy scale [8]. In the thin film form, TiO_2 is usually used in photovoltaic applications such as photoelectrochemical system (PEC) and dye sensitized solar cell (DSSC) for photon harvesting [4,9]. Moreover, TiO_2 in the thin film form offers the advantage of energy alignment between the energy position of the valance band edge and the redox species in the electrolyte by potential biasing the photoanodes. Several TiO_2 thin film deposition technique have been reported which include metal organic chemical vapor deposition (MOCVD) [10, 11], sol-gel [12], electrophoretic deposition [13], reactive RF sputtering [14]. Recently there are many applications of laser one of these applications in a thin film preparation field that called pulsed Laser deposition (PLD). With the pulsed laser deposition method, thin films are prepared by the ablation of one or more targets illuminated by a focused pulsed-laser beam. This technique was first used by smith and Turner in 1965 [15] for the preparation of semiconductor and dielectric thin films and was established due to the work of Dijkkamp and coworkers [16] on high-temperature superconductors in 1987. Their work already showed main characteristics of PLD, normally the stoichiometry transfer between target and deposited films, high deposition rate of about 0.1 nm per pulse and the occurrence of droplets on the substrate surface. The advantage of using PLD then other sputtering techniques is that PLD is quite easy to produce multilayered films of different material by sequential ablation of assorted targets. Besides, by controlling the number of pulses, a fine control of film thickness down to atomic monolayer can be achieved. The most important feature of PLD is that the stoichiometry of the target can be retained in the deposited film. In the said advantages of PLD, some short comings have been identified in using this deposition technique. In This paper TiO_2 film have been fabricated by pulsed laser deposition (PLD) method, which I widely used for the growth of oxide film because it allows for the stoichiometry of the synthesized material. The optical and structure of TiO_2 was studied.

II. EXPERIMENTAL DETAILS

A typical set-up for Pulse Laser Deposition (PLD) is schematically shown in Figure 1. In this study, TiO_2 was used as targets with diameter of 2 cm and thickness of 1cm was fixed at the top chamber. Glass substrate was used as substrate material to study the optical. The cleaning of the substrates was very necessary to ensure surface free from contamination films such as grease, absorber water.

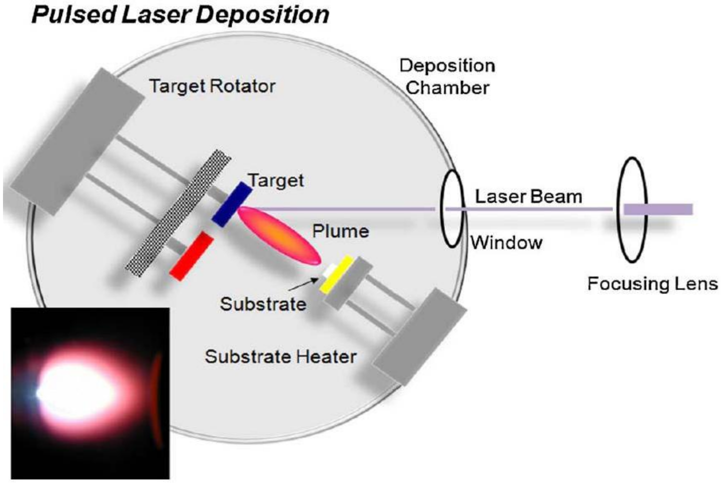

Figure 1: Schematic diagram of a typical laser deposition set-up.

The glass substrates were cut into standard sizes of 10 x 10 mm, were ultrasonically cleaned in acetone and dried into oven until it was. TiO_2 thin films were produced by Pulse Laser Deposition (PLD). In order to optimize the best location of the substrates on holder, the influence of the substrate to target distance on the structural and optical properties of TiO_2 thin films produced by Pulse Laser Deposition (PLD) in argon atmosphere was studied. The TiO_2 films were grown during 5 min onto glass microscope slides diametrically on the top plate substrate holder. The base pressure in the chamber and the working pressure were 2.0 x 10^{-5} mbar and 8 x 10^{-2} mbar, respectively. Pulse Laser Deposition (PLD) has become a preferred method for metal and semiconductors deposition. Providing high deposition rates and uniform coverage, dc magnetron sputtering provides the ability to quickly deposit large amounts of material, the optimums position on substrate holder of the substrates with respect to the target distance was determined. A series of films were synthesized under argon atmosphere with power 500 mJ and the working pressure (P_w) were kept constants and equal, P_w=8.0x10^{-2} mbar. In this study, a variety of characterization techniques were used to evaluate the structural, optical and electrical properties of the thin films. Of particular interest was the determination of the structure from X-ray diffraction, the film thicknesses from optical interference fringes. Optical parameters from UV-Visible absorbance spectrum in the spectral range (530 -850) nm. For determination of the thicknesses of films we can use optical interference fringes measurements can be rapid, accurate, and non-destructive. Interferometer is used as a quantitative method for the determination of certain optical parameters is very important in the characterization of the investigated films. Optical method was used for thickness measurements and in the flowing is explained in details:

The thickness of TiO_2 thin film was measured by using an optical interferometer method employing He-Ne laser 0.632 µm with incident angle 45° as shown schematically in Figure 2. This method depends on the interference of the laser beam reflected from thin film surface and then substrate, the films thickness t was determined using the following formula:

$$t = \frac{\lambda}{2} \cdot \frac{\Delta X}{X} \quad (1)$$

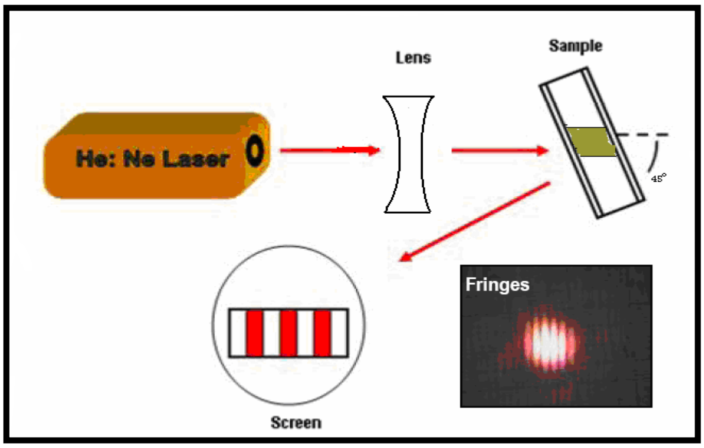

Figure 2: The schematic diagram of the film thickness measurement.

X-ray diffraction (XRD) is one of the most powerful techniques for qualitative and quantitative analysis of crystalline compounds. This experimental technique has long been used to determine the overall structure of TiO_2 thin films, including lattice constants, grain size identification of unknown materials, orientation of single crystals, and orientation of polycrystals. In this study thin films have been examined by X-ray diffraction (XRD) technique under the conditions power diffraction system with Cu-Kα X-ray tube (λ = 1.54056 Å) was used. The X-ray scans were performed between 2θ values of the X-ray diffraction (XRD) was recorded at a scanning rate of 0.08333° s^{-1} with the diffraction angle 2θ, range (20°-60°).

Optical measurements on the TiO_2 thin films were performed on a UV mate SP-8001 double beam spectrophotometer covering the wavelengths range (190-1100 nm) supplied by Metertech Corporation (Taipei, Taiwan). During scanning, a blank glass slide was placed in one of the beam's direction and another glass slide with film deposit was in the other beam's direction. Thus, the absorption spectrum displayed by the UV mate SP-8001 double beam spectrophotometer was as a result of the films deposited on the glass slide substrates.

III. RESULT AND DISCUSSION

X-ray diffraction investigates the structural type of the TiO_2 thin films prepared by pulse laser deposition. The XRD pattern for films deposited at room temperature showed that they are polycrystalline structure takes place. The XRD patterns for this TiO_2 films are presented in figure (3).

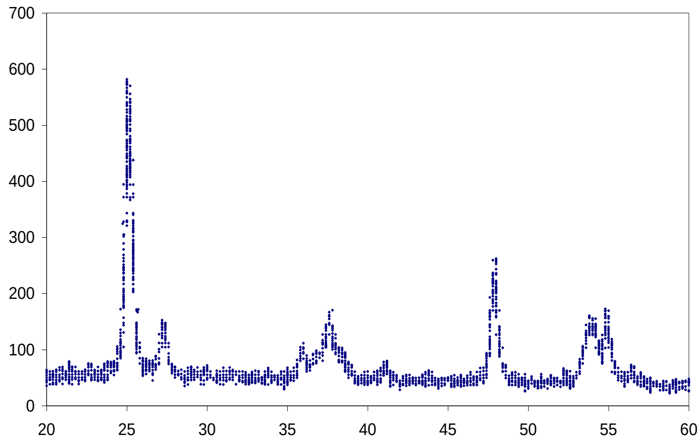

Figure 3: XRD pattern of TiO_2 thin film despite of glass substrate

The table 1 shown many dominant strongest peaks with their d spacing, FWHM, and diffraction angle values. The mean grain size of thin film calculated using the Scherer's equation [17]:

$$G = 0.94\, \lambda / \beta \cos\theta \qquad (2)$$

Where G is the average crystalline grain size, λ is the wavelength, β represents the full- width at half maximum (FWHM) in radian and θ is the Bragg diffraction angle in degree. The calculated values of grains size for TiO_2 thin film are shown in table 1.

Table 1: shows all peaks and its Bragg's angle, interplanar distance, and full width half at maximum

peak No.	(hkl)	2 Theta (deg)	d(Å)	FWHM (deg)	G (nm)
1	(101)	25.37	3.50	0.41	22.23
2	(110)	27.49	3.24	0.39	23.46
3	(103)	36.12	2.48	0.32	32.03
4	(004)	38.65	2.32	0.61	17.3
5	(111)	41.29	2.18	0.31	34.98
6	(200)	44.05	2.05	0.40	28.65
7	(211)	53.94	1.69	0.42	33.22

The optical characteristics which involve the absorption coefficient, the optical energy gap E_g, and the optical constants (i.e. refractive index n, extinction coefficient k, real dielectric constant E_r and imaginary dielectric constant E_i), were studied within the range (200-800) nm for TiO_2 thin deposited by PLD technique. The absorbance spectra for TiO_2 thin films are shown in figure (4). This spectrum reveals that the maximum absorption peak shifts towards the longer wavelength.

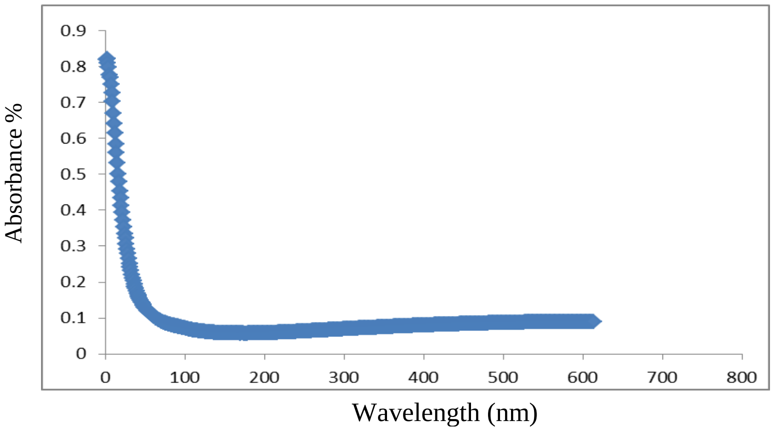

Figure 4: The optical absorbance of TiO_2 thin films.

The optical transmittance spectra for TiO_2 thin films are shown in figure (5). It is observed that the overall transmittance decreases with the increase of film thickness. This is due to the overall increase in the absorbance with the increase of film thickness. As shown from figure (5) rise and fall in the transmittance spectrum above the absorption edge are observed. This behavior is due to interference of the light transmitted through the thin film and the substrate.

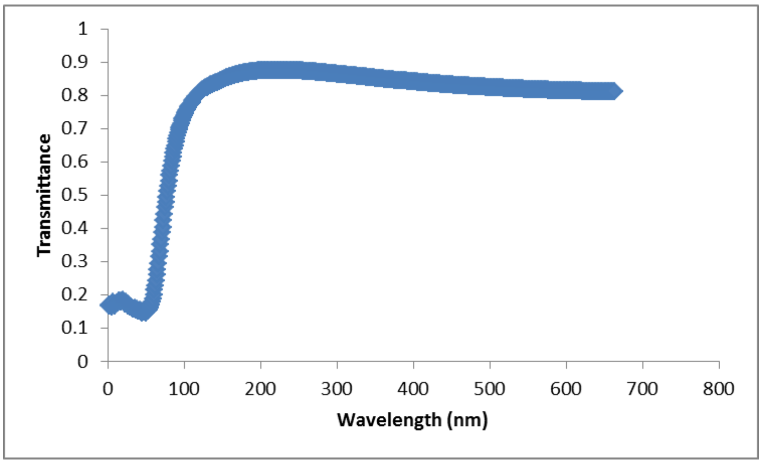

Figure 5: the optical transmittance of TiO_2 thin film

Figure (6) shows the variation of $(\alpha h\upsilon)^2$ as a function of $(h\upsilon)$ for TiO_2 thin films. It can be observed from this figure that the energy gap equal to 3.5 eV.

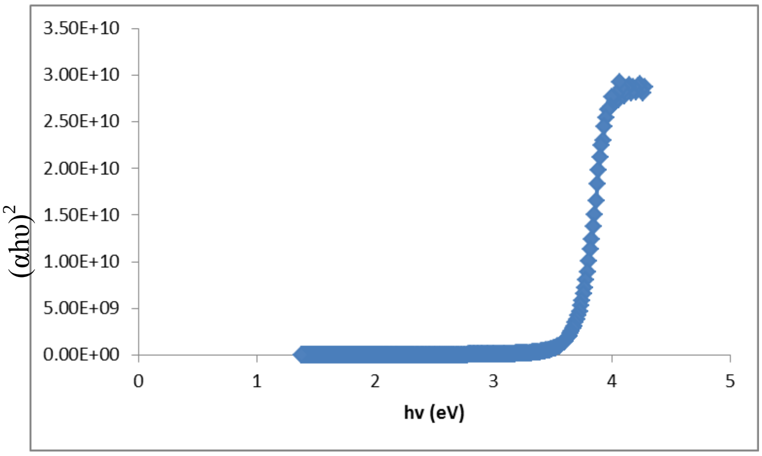

Figure 6: Variation of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for TiO_2 thin films.

Figure (7) shows the optical reflectance spectra of TiO_2 thin films. The reflectance spectrum represents the interference between the rays that are reflected from the film faces. As shown from figure (7), the reflectance of the film in visible region where wavelength (400-450) nm.

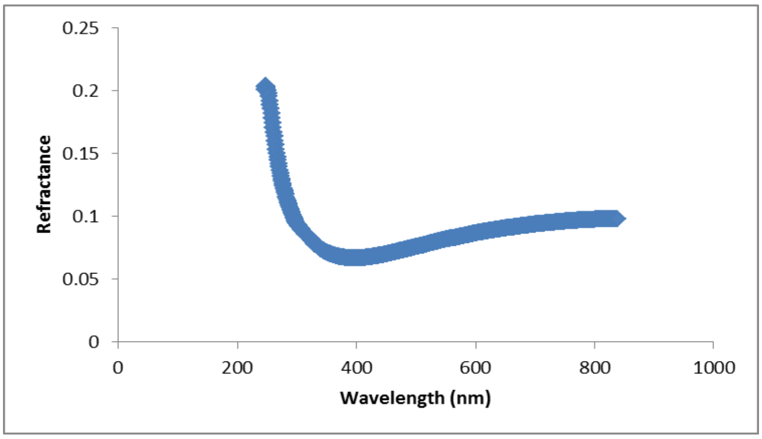

Figure 7: The Reflectance spectra for TiO_2 thin films at room temperature.

The optical constants which are include the of refractive index n, extinction coefficient k, the real E_r, and imaginary E_i parts of dielectric constants were determined from transmission and absorption spectra within the range (200 - 800) nm for Tio2 thin films prepared by PLD. Figure (8) shows the variation of the refractive index as a function of the wavelength for TiO_2 thin films. It indicates that the refractive index increases with increasing wavelength.

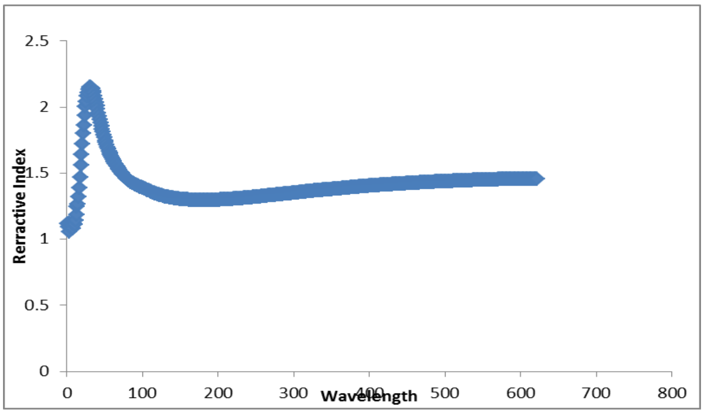

Figure 8: The Refractive Index for TiO_2 thin films at room temperature.

Figure (9) shows the variation of extinction coefficient as a function of wave length for TiO_2 Thin films. It is observed from this figure that the extinction coefficient decreases with increasing of wavelength. Also, it is observed from this figure that the extinction coefficient at wavelength 500 nm decreases with the wavelength, opposite to the variation of the refractive index, and this is due to the reason mentioned before. But the less values of extinction coefficient at 200 nm are due to the improve of the structure. Figures (10, 11) shows the variation of real ($\in_r$) and imaginary ($\in_i$) dielectric constants for TiO_2 thin films. One can observed that the variation of ε_r is similar trend to that of the refractive index because of the smaller value of k^2 in comparison with n^2, while the variation of ε_i mainly depends on the *k* value, which are related to the variation of absorption coefficient. ε_i represent the absorption of radiation by free carriers. It is observed from the figures that the real and imaginary dielectric constants decrease with the increase of the wavelength of the incident radiation and this behavior is due to the change of reflectance and absorbance.

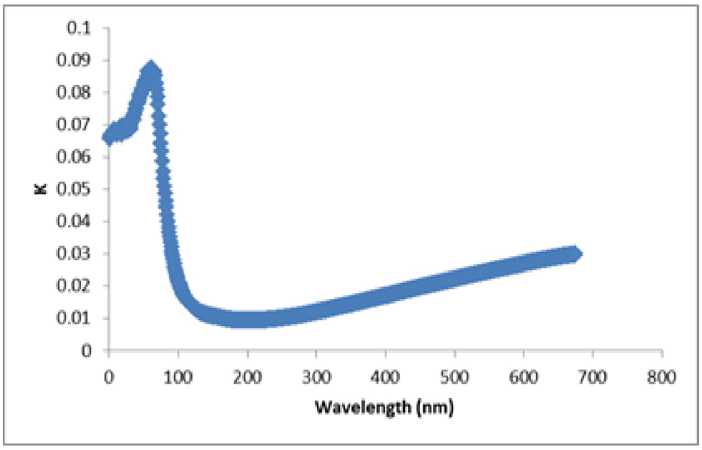

Figure 9: The Extinction coefficient for TiO_2 thin films at room temperature

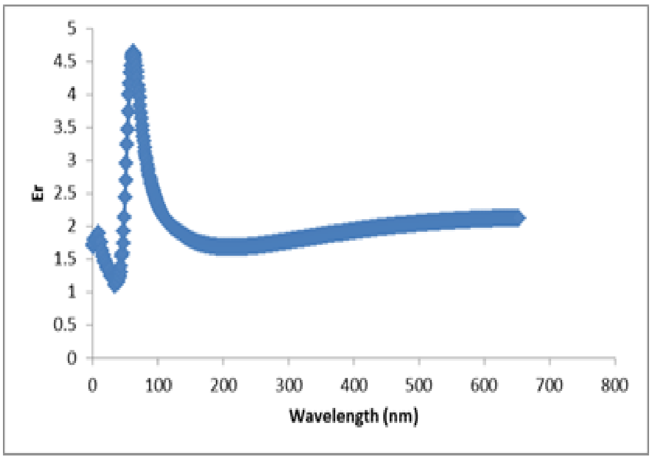

Figure 10: Real dielectric constant E_r for TiO_2 thin films

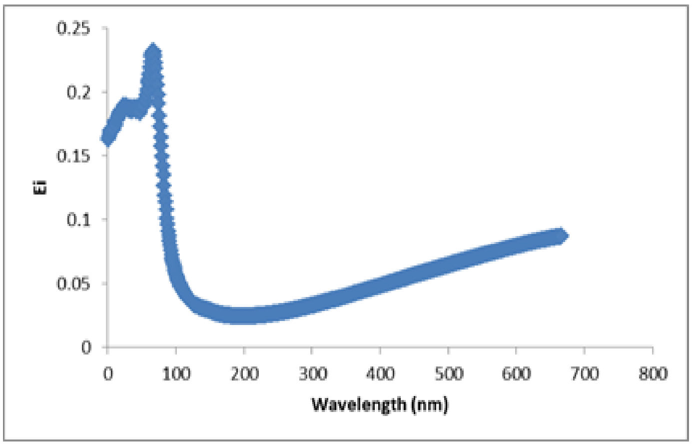

Figure 11: Imaginary dielectric constant E_i for TiO_2 thin films

IV. CONCLUSIONS

In this work we have reported the optical characteristic of TiO_2 thin films prepared by PLD. The optical transmittance measurement shows that the TiO_2 film has a flat surface, a high average transmittance over 80 % in the region and a direct band gap of 3.5 eV. The optical constants absorption coefficient, extinction coefficient and optical dielectric constant, of these films were determined using transmittance and refractance spectra.

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