

Effect of Annealing Temperature on the Optical Properties of TiO₂ Thin Films Prepared by Pulse Laser Deposition

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ABSTRACT. TiO₂ thin films were prepared by pulse laser deposition technique on glass substrates with laser power 700 mJ and 900 shot at distance 1cm under vacuum of 10⁻² mbar with different annealing temperature (273, 373, 423)K. The influences of the annealing temperature on the optical properties of TiO₂ thin films were mainly investigated. TiO₂ is a wide band gap n-type semiconductor that has a wide range of applications. It was found that the optical properties of TiO₂ thin films were dependent on the annealing temperature. The values of optical energy gap decreases from (3.4 to 3.2) eV when increasing annealing temperature. The optical constants such as refractive index, extinction coefficient, real and imaginary dielectric constants as a function of wavelength were determined.

1. INTRODUCTION

Titanium dioxide (TiO₂)(titania) is a cheap, non-toxic and one of the most efficient semiconductor photocatalysts for extensive environmental applications because of its strong oxidizing power, high photochemical corrosive resistance and cost effectiveness [1]. Due to these inherent properties, TiO₂ is the most suitable candidate for degradation and complete mineralization of toxic organic pollutants in water [1,2]. It is well known that TiO₂ exists in three crystalline structures: rutile, anatase and brookite [3,4]. 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 [5]. In principle, transition metal with proper oxidation state replace some of the Ti (IV) from lattice producing an impurity state that reduces the band gap of TiO₂.

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, anti reflection coatings, optical waveguides, photonic crystals, devices based on metal etc [6]. Many deposition methods have been used to prepare TiO₂ thin films, such as electron-beam evaporation [7], ion-beam assisted deposition [8], DC reactive magnetron sputtering [9], RF reactive magnetron sputtering [10], sol-gel dip coating method [11], sol-gel spin coating method [12], chemical vapor deposition [13], plasma enhanced chemical vapor deposition [14] and pulsed laser deposition (PLD) [15]. Among these methods, PLD technique has been widely used for growing oxide films because it allows for stoichiometry of the synthesized material. In this work, we study the effect of annealing temperature on the optical properties of TiO₂.

2. EXPERIMENTAL

The deposition was carried out using a Q switched Nd:YAG laser at 1064 nm (900 shot and laser fluency 700 mJ/cm²). The studied films were prepared from pure TiO₂ target film were grown by pulsed laser deposition on glass substrates, kept distance of 1 cm from the TiO₂ target. For film deposition, all substrates (the glass substrates 8 × 2.5 cm² with 1 mm thickness) were cleaned in acetone and methanol solutions in an ultrasonic bath for 30 minutes. Then compress the mixture

under 5 Ton (homemade compressor) to get the final pellet of TiO_2 powder of 2.5 cm diameter. The optical properties of the films were studied by recording the absorption spectra from UV-VIS spectrophotometer at room temperature in the wavelength range of 200- 1100 nm.

3. RESULTS AND DISCUSSION

The optical properties of TiO_2 thin film prepared by PLD method with various annealing temperature (273, 373, 423)K and average thickness 500 nm were investigated using UV-Visible spectrophotometer in the region of (200-1100) nm. From Fig.1 it can observe that the transmittance of the TiO_2 thin film decreases with increasing annealing temperature and then dropped, this may be due to the increase in film homogeneity, with the increase of the surface roughness promoting the increase of the surface scattering of the light by increasing the columnar growth with needle and rod like shape [7,16]. In addition, the transmittance increase with increasing wavelength for all prepared thin films.

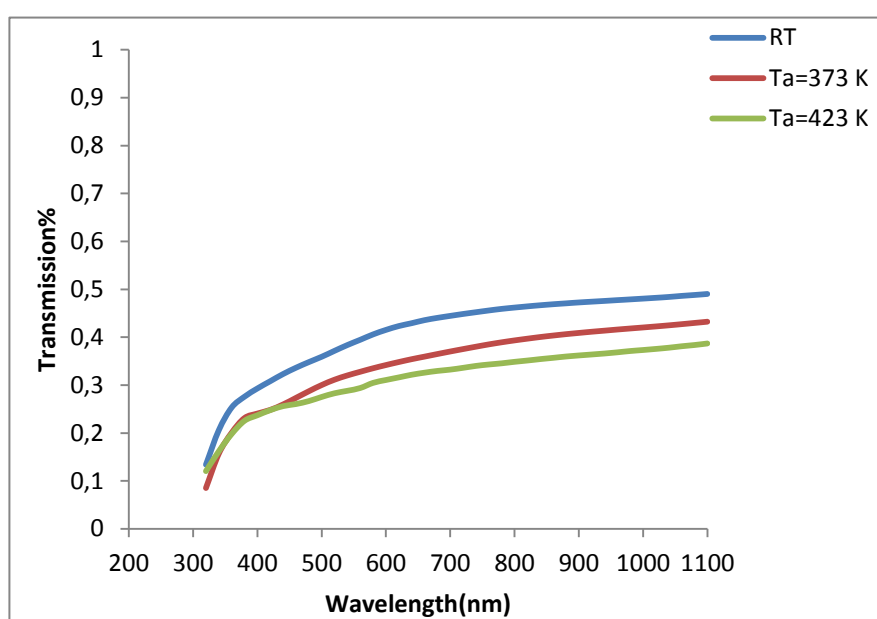


Fig.1: Variation of transmittance spectra as a function of Wavelength for TiO_2 thin films with different annealing temperatures.

The absorbance spectra of the TiO_2 thin film deposited on glass substrate measured with various annealing temperature (273, 373, 423) K is shown in Fig.2. In high-energy spectral range, where the film is strongly absorbent, and the absorbance of TiO_2 thin film increases with increasing annealing temperature for all prepared thin films.

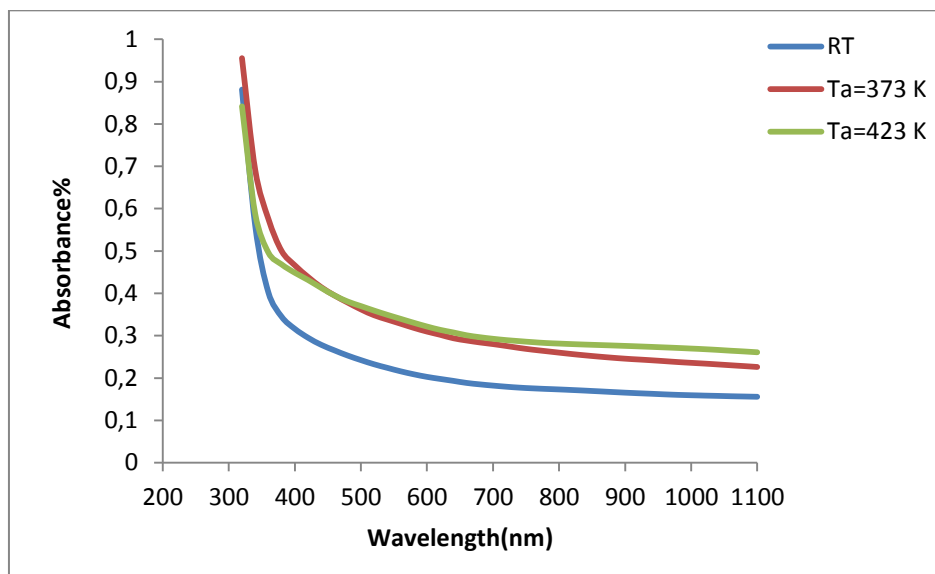


Fig.2: Variation of the absorbance spectra as a function of wavelength for TiO₂ thin films at different annealing temperature.

The absorption coefficient α was determined from the region of high absorption at the fundamental absorption edge of the film. The variation of the absorption coefficient versus the wavelength for TiO₂ with various annealing temperature (273, 373, 423) K is shown in the Fig.3. The absorption coefficient (α) is increased with the increasing annealing temperature. This can be linked with increase in grain size and it may be attributed to the light scattering effect for its high surface roughness [17].

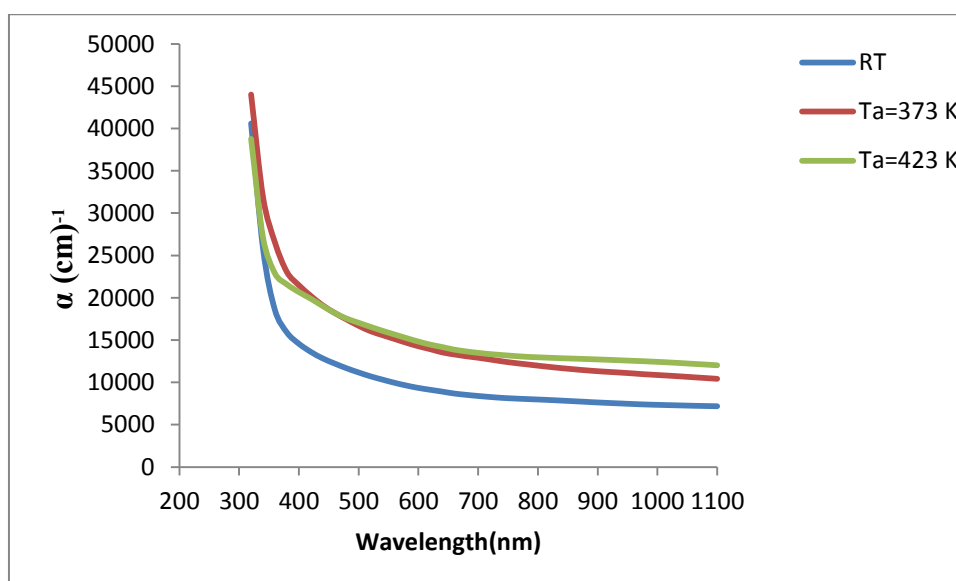


Fig. 3: Variation of the absorption coefficient spectra as a function of wavelength for TiO₂ thin films at different annealing temperature.

In order to calculate the band gap energies of TiO₂ thin films, the plot of $(\alpha h\nu)^2$ as a function of the energy of incident radiation has been plotted in Fig.4. The energy band gap is obtained from intercept of the extrapolated linear part of the curve with the energy axis at $(\alpha h\nu)^n = 0$ the intercept with x-axis equal to E_g . it can be observe that direct band gap of the TiO₂ films decreases from (3.4 eV –3.2 eV) as the annealing temperature increases from RT to 423 K. From Table (1) and the figure, it can be observed that (E_g) was decreased with the increasing of annealing temperature for all films. Annealing led to increased levels of localized 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, or can be attributed decrease energy gap to the increased size of particles in the films [18].

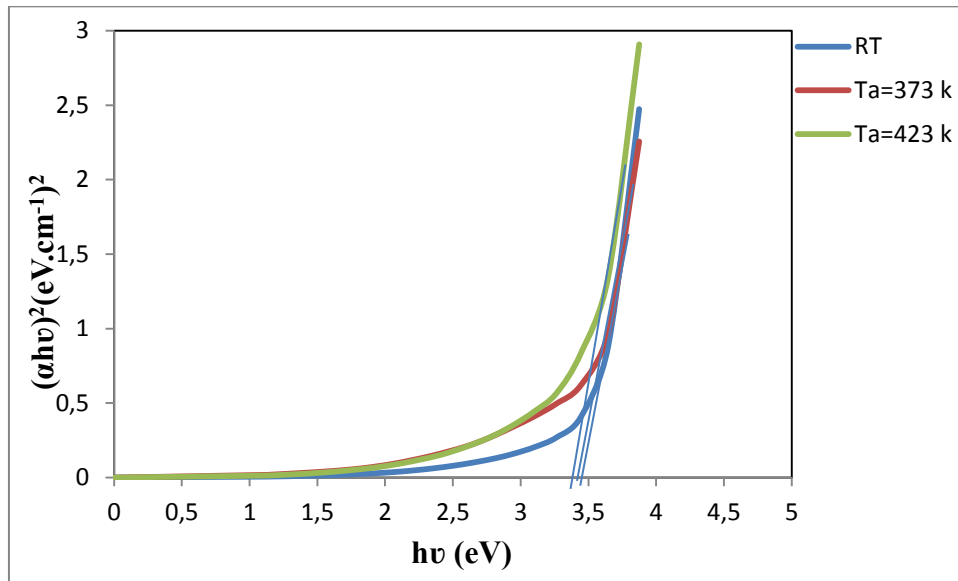


Fig.4: A plots of $(\alpha h\nu)^2$ verses photon energy ($h\nu$) of TiO_2 thin films at different annealing temperatures.

Table 1: The obtained result of optical energy gap of TiO_2 thin films at different annealing temperatures.

Temperature (K)	Optical energy gap (eV)
RT	3.4
373	3.3
423	3.2

Optical constants included refractive index (n), extinction coefficient (k), and real (ϵ_r) and imaginary (ϵ_i) parts of dielectric constant. The refractive index can be calculated from the following equation [19].

$$n = \left[\frac{4R}{(R-1)^2} - k^2 \right]^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \quad (1)$$

Where R is the reflectance and given by the equation [20].

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (2)$$

The variation of the refractive index versus wavelength in the range (200-1100) nm for TiO_2 thin films with various annealing temperature (273, 373, 423) K, is shown in Fig. 5. It can notice from the figure that the refractive index, in general, increases slightly with increasing of T_a . This behavior can be explained on the basis of that increasing of T_a to make less density (lowering the packing density) which in turn increases propagation velocity of light through them which results in increasing of n values, since n represent the ratio of light velocity through vacuum to velocity through any medium.

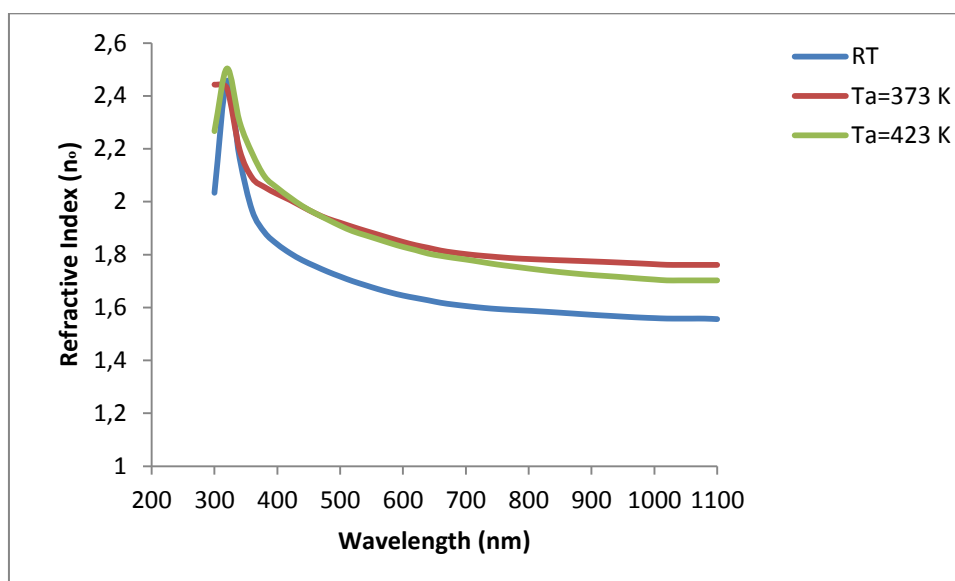


Fig.5: Variation of refractive index with wavelength of the TiO₂ thin films at different annealing temperature.

The behavior of the extinction coefficient of TiO₂ films at different annealing temperatures shown in Fig.6. It can observe from the figure that the extinction coefficient, in general, increases with increasing of annealing temperature.

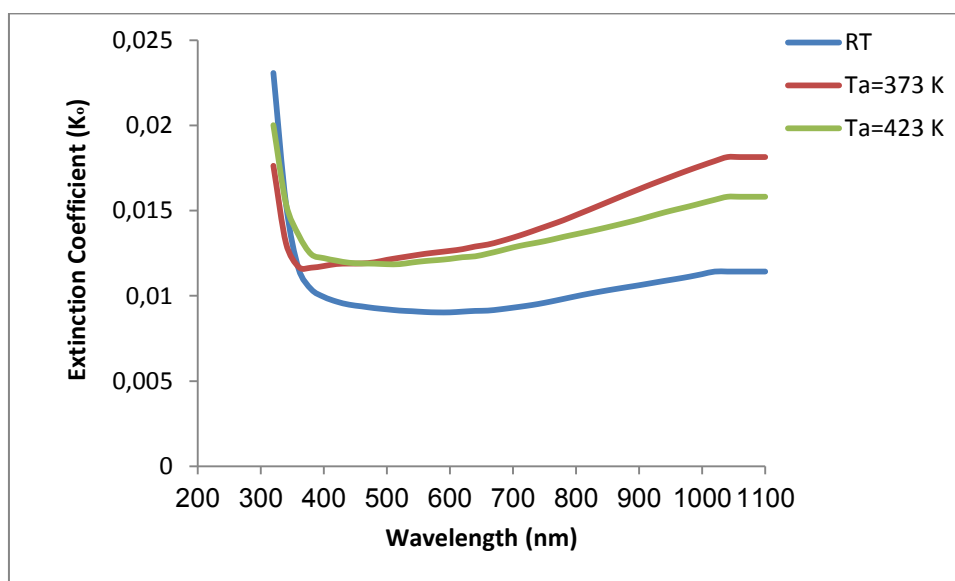


Fig.6: Variation of Extinction coefficient with wavelength of the TiO₂ thin films at different annealing temperature.

The variation of the real (ϵ_r) and imaginary (ϵ_i) parts of dielectric constant values versus wavelength in the range (200-1100) nm for TiO₂ with various annealing temperature (273, 373, 423)K as shown in Figs.(7,8). The behavior of ϵ_r is similar to that of the refractive index because of the smaller value of k^2 compared with n^2 according by relation $\epsilon_r = (n^2 - k^2)$ while ϵ_i mainly depends on the k values. It is found that ϵ_r and ϵ_i increased with increasing of annealing temperature.

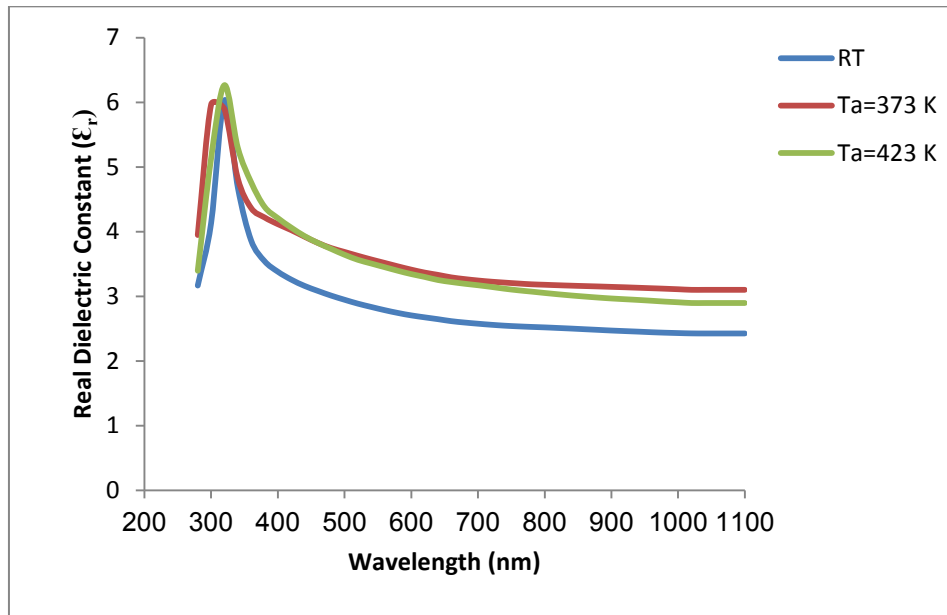


Fig.7: Variation of real dielectric constant with wavelength of the TiO₂ thin films at different annealing temperature.

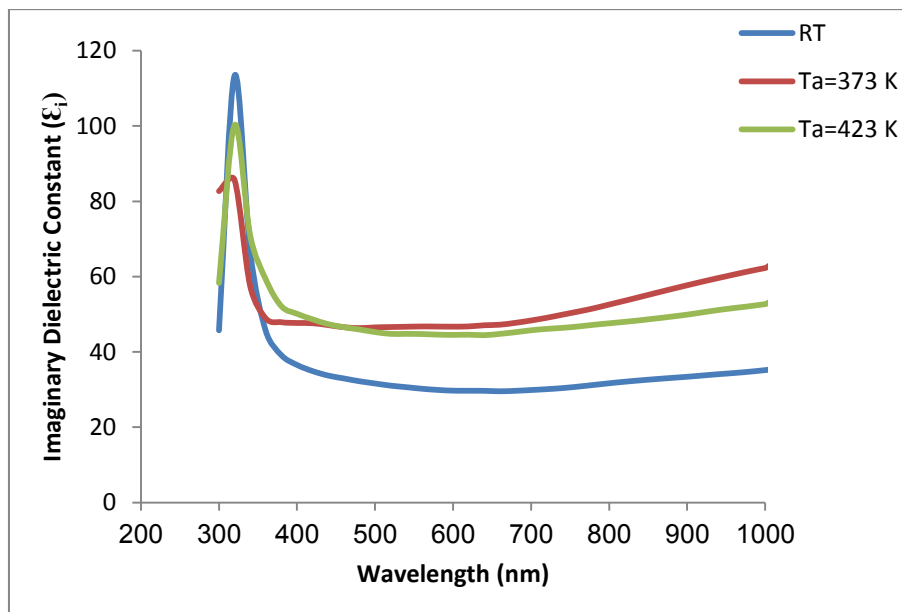


Fig.8: Variation of imaginary dielectric constant with wavelength of the TiO₂ thin films at different annealing temperature.

4. CONCLUSIONS

TiO₂ thin films were deposited on glass substrate by applying a versatile PLD technique with synchronized laser (Nd:YAG). The dependences of optical properties of TiO₂ thin films in RT and different annealing temperatures were investigated. Optical properties of TiO₂ thin films deposited at different temperature are presented. Band gap obtained for these films is in the range of 3.4–3.2 eV. With the temperature increased for (273, 373 and 423) K, the optical transmittance reduced and the band gap decreased. The refractive index and extinction coefficient increased slightly with increasing of annealing temperatures for all samples. The variation of the real and imaginary parts of the dielectric constant have similar trend as for n and k respectively.

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