Annealing Effect on the Growth of Nanostructured TiO_2 Thin Films by Pulsed Laser Deposition (PLD)

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ABSTRACT

In this work, Nanostructured TiO_2 thin films were grown by pulsed laser deposition (PLD) technique on glass substrates at 300 °C. TiO_2 thin films were then annealed at 400-600 °C in air for a period of 2 hours. Effect of annealing on the structure, morphology and optical properties were studied. The X-ray diffraction (XRD) and Atomic Force Microscopy (AFM) measurements confirmed that the films grown by this technique have good crystalline tetragonal mixed anatase and rutile phase structure and homogeneous surface. The study also reveals that the RMS value of thin films roughness increased with increasing annealing temperature .The optical properties of the films were studied by UV-VIS spectrophotometer. The optical transmission results shows that the transmission over than ~65% which decrease with the increasing of annealing temperatures. The allowed indirect optical band gap of the films was estimated to be in the range from 3.49 to 3.1 eV. The allowed direct band gap was found to decrease from 3.74 to 3.55 eV with the increase of annealing temperature. The refractive index of the films was found from 2.27 -2.98 at 550nm. The extinction coefficient increase with annealing temperature.

Keywords: Titanium dioxide, Pulsed laser deposition, Structural, Morphology, Optical properties, TiO_2 films

تأثير التلوين على انماء الاغشية الدقيقة ل(TiO_2) ذات التركيب الثانوي بواسطة تركيب الليزر النبضي

الخلاصة

في هذه البحث، تم انماء أغشية اوكسيد التيتانيوم (TiO_2) النانوية بواسطة تقنية ترسيب الليزر النبضي (PLD) على قواعد زجاجية في درجة حرارة ٣٠٠ مئوية .ومن ثم لدنت أغشية TiO_2 الرقيقة من ٤٠٠ الى ٦٠٠ درجة مئوية في الهواء لمدة ساعتين . وتم دراسة تأثير التلدين على

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تركيب وطبوغرافية السطح والخصائص البصرية. من قياسات حيود الأشعة السينية (XRD) ومجهر القوة الذرية (AFM) اثبت بأن الاغشية المنمات بهذه الطريقة لها تبلور جيد وذات تركيب رباعي وخليط من طورين الأناتاس والروتيل وذات سطح متجانس. وتظهر الدراسة بأن قيم RMS للأغشية الرقيقة والخشونة تزداد مع زيادة درجة الحرارة التلدين .وتم دراسة الخصائص البصرية للأغشية في مطياف النفاذية للأشعة المرئية وفوق البنفسجية (قيست بواسطة مطياف UV-VIS). نتائج النفاذية الضوئية تظهر بأن هنالك نفاذية أكثر من~ 65٪ والتي تقل مع زيادة درجات الحرارة التلدين .فجوة الطاقة البصرية المسموحة الغير مباشرة الأغشية قدرة بحدود من ٣,٤٩ الى ٣,١ الكترون فولت. ووجد ان فجوة الطاقة البصرية المسموحة المباشرة تقل من ٣,٧٤ الى ٣,٥٥ إلكترون فولت بزيادة درجة حرارة التلدين. ووجد ان معامل الانكسار للأغشية تتراوح من ٢,٢٧ الى ٢,٩٨ عند الطول الموجي ٥٥٠ نانومتر. وان معامل الخمود يزداد بزيادة درجة حرارة التلدين.

INTRODUCTION

Over the last few decades, titanium dioxide (TiO_2) has been widely investigated recently for its interesting optical properties, electronic properties and good stability in the adverse environment. For its high refractive index, wide band gap and chemical stability, polycrystalline TiO_2 films are used for a variety of applications such as optics industry [1], dyesensitized solar cells [2], dielectric applications [3], self-cleaning purposes [4] and photocatalytic layers [5]. The highly transparent TiO_2 films have been widely used as antireflection coatings for increasing the visible transmittance in heat mirrors [6]. A heat mirror is a device that exhibits high transmittance at short wavelength combined with high reflectance at long wavelength, has been developed for reflecting the solar heat in a warm climate or to prevent the escape of indoor heating in a cold climate. TiO_2 is one of the mostly used materials for the purpose of antireflection coatings [7-8]. TiO_2 can exist as an amorphous layer and also in three crystalline phases: anatase (tetragonal), rutile (tetragonal) and brookite (orthorombic). Only rutile phase is thermodynamically stable at high temperature. TiO_2 thin films can be prepared by different techniques such as, reactive magnetron sputtering [5], Sol-gel methods [9, 10], chemical vapor deposition [11], and pulsed laser deposition (PLD) [12] have been used to fabricate TiO_2 films. Among these methods, PLD technique has been widely used for growing oxide films because it allows for stoichiometry of the synthesized material [12]. The properties of the titanium dioxide films depend not only on the preparation techniques but also on the deposition conditions. Heat-treatment is one of the utilized ways to obtain better optical properties of TiO_2 films [13]. In the present paper, we report preparation and deposition of nanocrystalline TiO_2 mixed phase (anatase and rutile) thin films by pulsed laser deposition technique. Besides the films were taken for further annealing treatment. Hence, the effects of heat-treatment on structural, morphology and optical properties were investigated in this paper.

Experimental details

Titanium dioxide from ASDGF Company with a titanium target of 99.99% purity on glass slides as substrates. The powder was pressed under 5 ton to form a target with 2.5 cm diameter and 0.4 cm thickness. Glass slides each of 3 x 2 cm^2.

They were cleaned by alcohol with ultrasonic waves produced by Cerry PUL 125 device for 10 minutes in order to remove the impurities and residuals from their surfaces. Thin films were deposited using pulsed laser deposition by employing a Q switched Nd: YAG laser at wavelength 532 nm with 0.4 J/cm^2 of energy density, pulse width 10 ns and repetition frequency 6 Hz. Uniform ablation ensured by rotating the target at constant speed as in Figure (1). The focused Nd:YAG SHG Q-switching laser beam incident on the target surface making an angle of 45° with it. The films were deposited on glass substrate at temperatures 300 °C. The pulsed laser deposition experiment was carried out inside a vacuum chamber generally in (10^{-2} Torr) vacuum conditions. The substrates deposited at 300 °C temperature with TiO_2 were annealed at 400 ˚C, 500 °C and 600 °C using an electric furnace for 2 h in air. The crystallinity of the prepared films was analyzed using X-ray Diffraction (XRD) measurements (Shimadzu 6000 made in Japan) using Cu Kα radiation at 1.5406 Å and operating at an accelerating voltage of 40 kV and an emission current of 30 mA. Data were acquired over the range of 2θ from 20° to 60°. The XRD method was used to study the change of crystalline structure. For morphological investigations, AFM images were recorded using Nanoscope scanning probe microscope controller in a tapping mode. The AFM images were used to observe the surface roughness and topography of deposited thin films. Optical measurements were conducted in the wavelength range 300 nm to 900 nm using a double beam UV-Visible spectrophotometer (UV-1650 UV-Visible Recording Spectrophotometer) Shimadzu made in Japan was used to measure the transmittance and absorption of TiO_2 deposited. The transmittance and reflectance data can be used to calculate absorption coefficients of the films at different wavelength. Which have been used to determine the band gap E_g .The Film thickness measurements by optical interferometer method have been obtained.

Results and Discussion

Structural Properties

The X-ray diffraction patterns of TiO_2 thin films which were as-deposited at 300 °C temperature and annealed at 400 – 600 °C temperatures with a fixed annaling time of 2 h in air. The effect of annealing temperature on the crystallinity of TiO_2 can be understood from the Figure (2).

The X-ray spectra show well-defined diffraction peaks showing good crystallinity, It was found that all the films were polycrystalline. The diffraction peaks are in good agreement with those given in JCPD data for TiO_2 anatase and rutile. It was observed that the intensities of the peaks of few TiO_2 planes increased slightly with the increase of annealing temperature. This means that TiO_2 films have been crystallized in a tetragonal mixed anatase and rutile form. However, the Full Width at Half Maxima FWHM of the (101) peaks was hardly changed with increasing film annealing temperature, this goes in agreement with the previous work [14].

The TiO_2 (101) peak of anatase-type structure is considered to be suitable for photocatalytic applications [15]. The grain size of all TiO_2 samples sintered at 400 °C to 600 °C was calculated using Scherer's equation and it is in the range of ~ (19

– 31.85) nm, revealing a fine nanocrystalline grain structure. Can be seen in Table (1).

Atomic force microscopy (AFM)

The surface morphology of all the TiO_2 films is presented by AFM images in tapping mode. The surface morphology reveals the Nano-crystalline TiO_2 grains. Figure (3) shows the AFM images of the TiO_2 thin films deposited at 300 ºC and annealed at different temperatures (400, 500 and 600) ºC.

The surface morphology of the TiO_2 thin films as observed from the AFM micrographs proves that the grains are uniformly distributed within the scanning area (10 µm x 10 µm). Annealing up to 400 °C impart a significant change in structure.The R MSroughness also increased with increasing annealing temperatures. Annealing temperature certainly changes the topography drastically as shown in Table (2).

Optical Properties

Figure (4) shows the transmittance spectra of TiO_2 films. It is found that average transmittance of as-deposited TiO2 films is about 65% in the near-infrared region with respect to reference; It is obvious that the transmittance decreases with the increase of annealing temperature. The blank glass substrate. Films annealed at 600 °C shows a significant decrease in the range from 350nm to 800nm transmittance. This is in consistent with the increase of the surface roughness promoting the increase of the surface scattering of the light [16]. TiO_2 films annealed at a higher temperature shows a lower transmittance. Because annealing treatment causes a film surface to be more rough which scatters light [16].

The curves of refractive index and extinction coefficient for as-grown and annealed TiO_2 films are shown in Figure (5) and Figure (6). Here, it is found that the refractive index at 550 nm for as deposited, annealed at 400 °C, 500 °C and 600 °C are 2.27, 2.51, 2.66 and 2.98 respectively. This trend shows an increase of the value of refractive index with higher annealing temperature. The increase may be attributed to higher packing density and change in crystalline structure. From Fig. 6, the extinction coefficient is also found to increase as the treatment temperature is increased. In the visible/near infrared region. Few researchers reported that the as-deposited or annealed TiO_2 films had refractive index in the range of 2.10-2.90 and annealing treatment caused refractive index to increase due to the enhancement of crystallization [17, 18].

Optical band gap was determined using the relation [19].

$$\alpha h\nu = A(h\nu - E_g)^r \qquad \dots (1)$$

Where α is the absorption coefficient, hν is the photon energy, E_g is the optical band gap, A is a constant which does not depend on photon energy and r has four numeric values (1/2 for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions). In this work, indirect and direct band gap was determined by plotting $(\alpha h\nu)^{1/2}$ vs. hν and $(\alpha h\nu)^2$ vs. hν curves respectively, with the extrapolation of the linear region to low energies. From Figure (7), it was observed that indirect optical band gap decreases from 3.49 eV to 3.1 eV with the increase of annealing temperature up to 600 °C .This result is in agreement with earlier study [15].

For evaluating allowed direct band gap,the curves used are shown in Figure (8).The direct optical band gap for the as-deposited film and annealed at 400 °C, 500 °C and 600 °C are 3.74, 3.7, 3.68 and 3.55 eV respectively. Here the decrease of direct band gap with the increase of annealing temperature is also observable. This result is in agreement with earlier study [14].

The energy gap values depend in general on the films crystal structure, the arrangement and distribution of atoms in the crystal lattice also affected by crystal regularity [20].

CONCLUSIONS

Nanostructured titanium dioxide thin films were prepared by pulsed laser deposition techniques on the glass substrate. The effect of annealing temperature on structure, morphology and optical properties of TiO_2 thin films were studied by XRD, AFM and UV-Visible measurements. The XRD results reveal that the deposited thin film and annealed at 400 °C of TiO_2 have a good Nanocrystalline tetragonal anatase phase structure. Thin films annealed at 500 °C and 600 °C have mixed anatase and rutile phase structure. The AFM results showed the slow growth of crystallite sizes for the as-grown films and annealed films from 400 to 600 °C. The transmittance decreased with increasing annealing temperature. The film annealed at 600 °C has the least transmittance among the films. For as-grown and annealed TiO_2 films, the refractive index at 550 nm wavelength increases and ranges from 2.27 to 2.98 which is close to bulk TiO_2 material. The extinction coefficient increases with the increase of treatment temperature. It is observed that the allowed indirect optical band gap of the films decreases from 3.49 to 3.1 eV with the increase of annealing temperature. And the allowed direct band gap is found to decrease from 3.74 to 3.55 eV.

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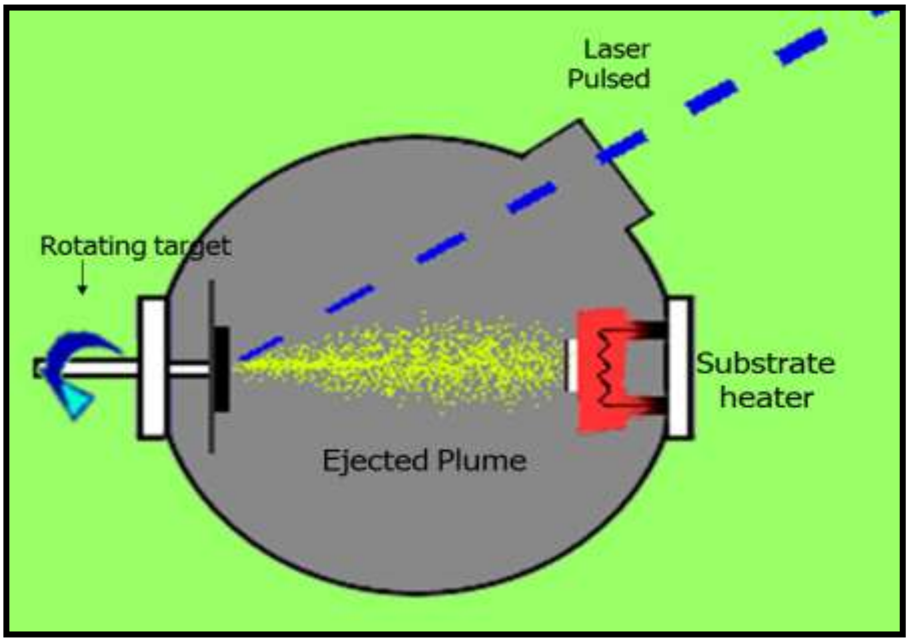

Figure (1) Schematic diagram of pulsed laser deposition set-up.

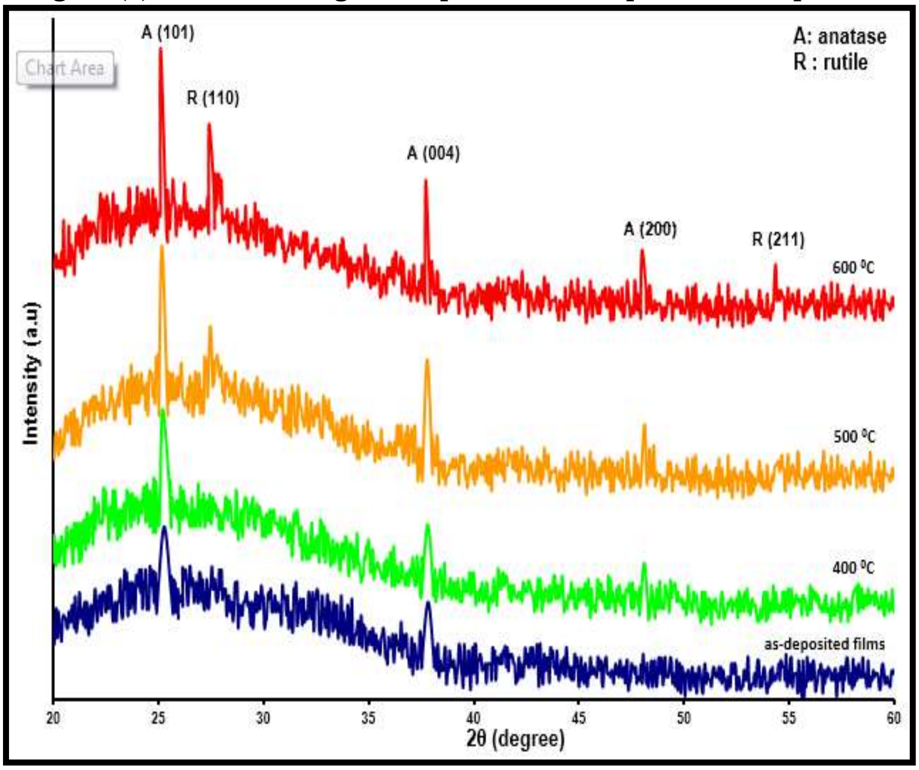

Figure (2) XRD patterns of TiO_2 films deposited at 300 °C temperature and annealed at 400 °C, 500 °C and 600 °C.

Table (1) The obtained result of the structural parameters from XRD for TiO_2 thin film.

Temp. ºC	*2θ (degree)*	*(hkl)*	*Main grain size (nm)*
As-deposited at 300	**25.27**	**A(101)**	**19.02**
	37.83	**A(004)**	**19.94**
400	**25.2**	**A(101)**	**20.19**
	37.81	**A(004)**	**21.27**
	48.1	**A(200)**	**22.16**
500	**25.17**	**A(101)**	**24.16**
	37.79	**A(004)**	**21.94**
	48.12	**A(200)**	**25.99**
	27.47	**R(110)**	**25.59**
600	**25.11**	**A(101)**	**28.25**
	37.72	**A(004)**	**30.43**
	48	**A(200)**	**26.88**
	27.41	**R(110)**	**27.13**
	54.35	**R(211)**	**31.85**

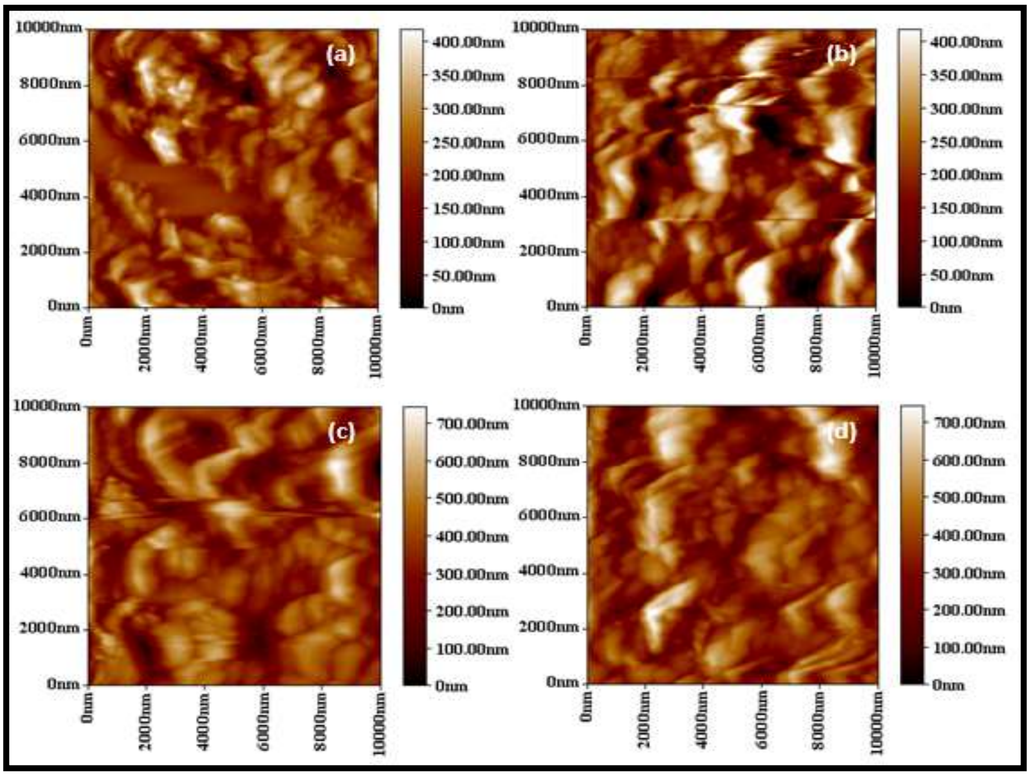

Figure (3) AFM images of TiO_2 films deposited at 300 °C temperature and annealed at different temperatures: (a) As-deposited, (b) 400 °C, (c) 500 °C and (d) 600 °C.

Table (2) Morphological characteristics from AFM images for TiO_2 thin film.

Temp. °C	Roughness average (nm)	Root Mean Square (RMS) (nm)
As-deposited at 300	46.5	60.5
400	76.6	95
500	84.3	105
600	88.6	114

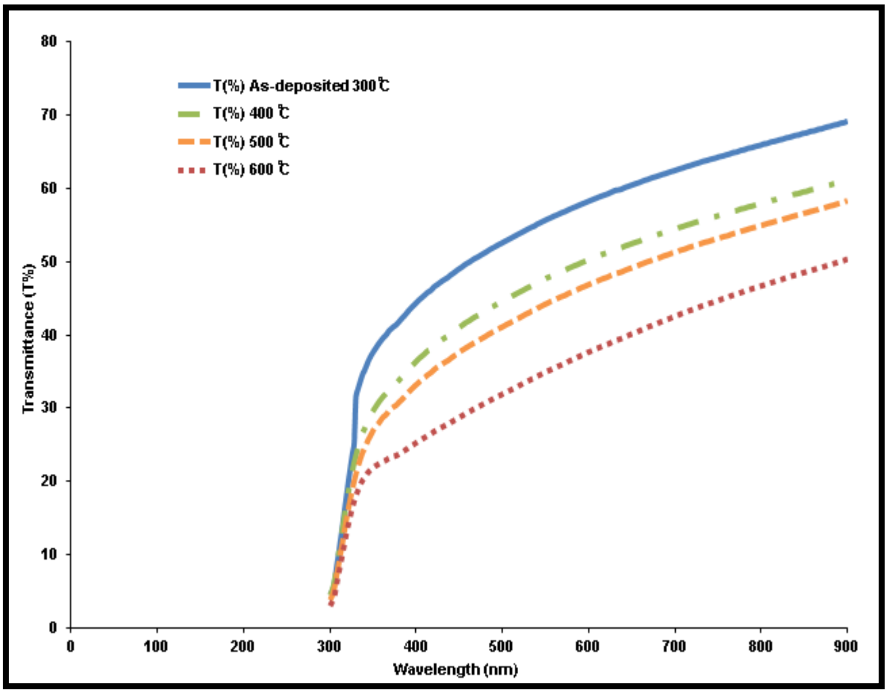

Figure (4) Transmittance spectra of TiO_2 films: (a) as-deposited 300 °C, (b) annealed at 400 °C, (c) 500 °C and (d) 600 °C.

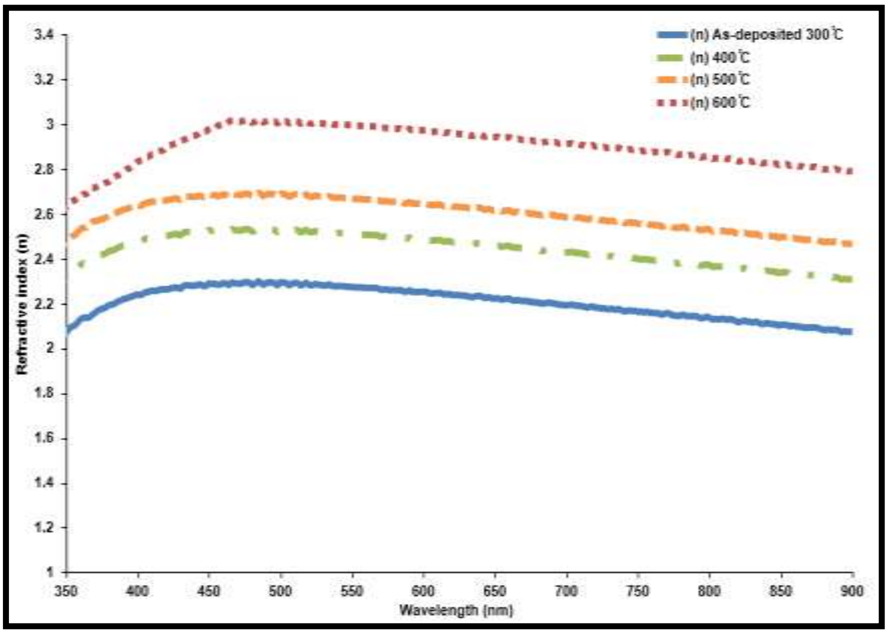

Figure (5) Refractive index of TiO_2 films: (a) as-deposited 300 °C. (b) Annealed at 400 °C. (c) 500 °C and (d) 600 °C.

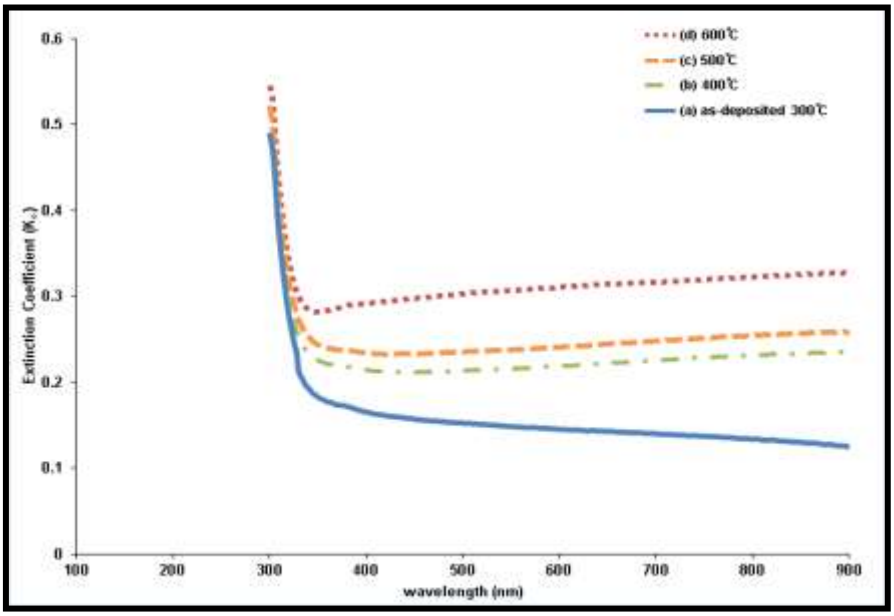

Figure (6) Extinction coefficient of TiO_2 films: (a) as-deposited 300 °C. (b) Annealed at 400 °C , (c) 500 °C and (d) 600 °C.

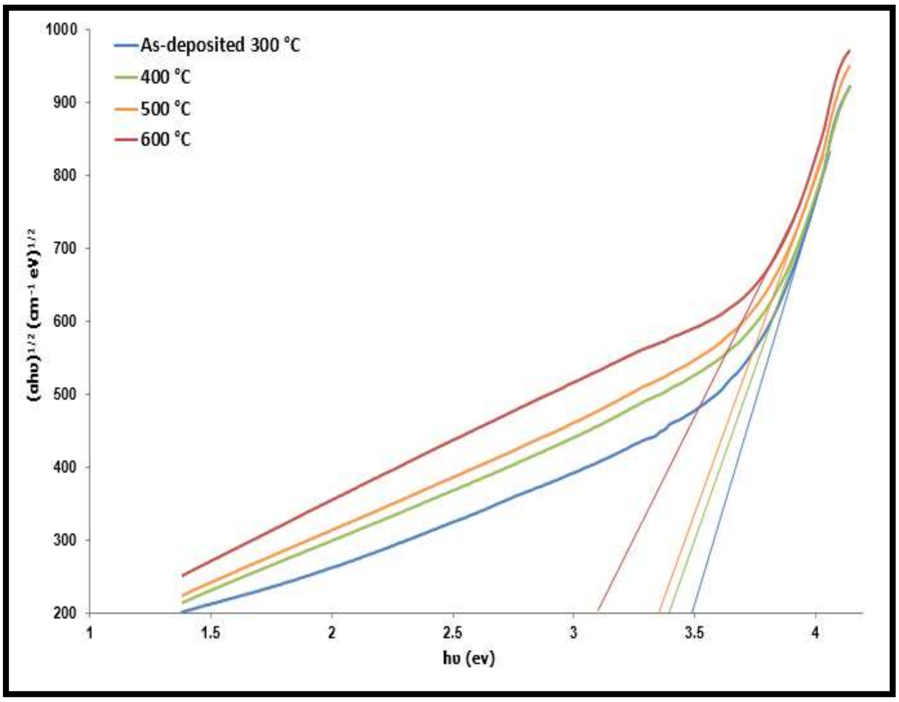

Figure (7) Variation of $(\alpha h \nu)^{1/2}$ versus energy curves of TiO_2 films (a) as-deposited at 300 °C. (b) Annealed at 400 °C, (c) 500 °C and (d) 600 °C.

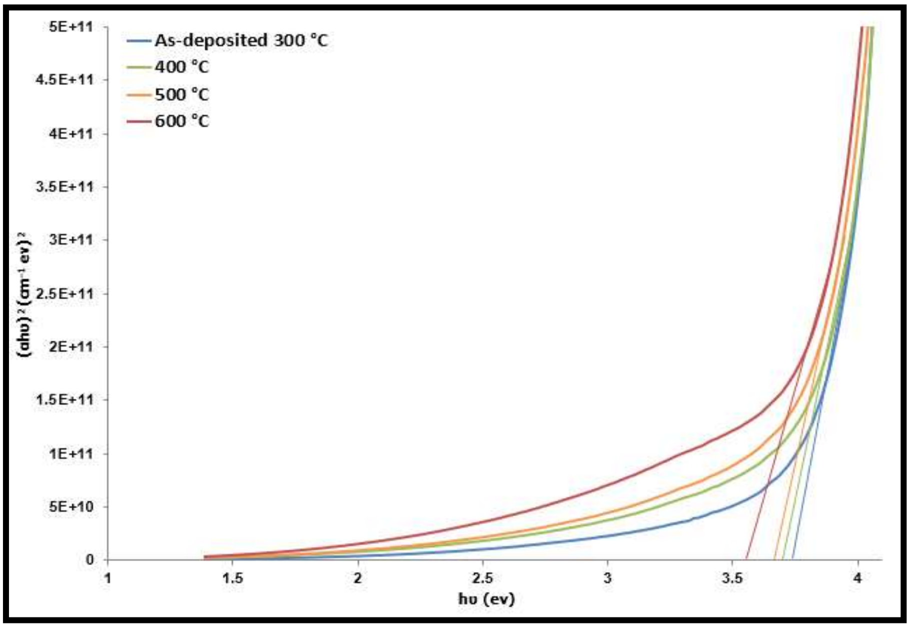

Figure (8) Variation of $(\alpha h \nu)^2$ versus energy curves of TiO_2 films: (a) as-deposited at 300 °C (b) annealed at 400 °C, (c) 500 °C and (d) 600 °C.