Effect of Argon Gas on the Structure and Optical Properties of Nano Titanium Oxide Prepared by PLD

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Abstract

In this research the effect of laser energy by using argon gas on the some physical properties of semiconductor film of TiO_2, was studied used Q-Switch Nd:YAG laser in different energies (600-1000) mJ with temperature 100 ^{0}C for glass substrate under vacuum nearly 10^{-3} mbar. From X-ray diffraction we found the film characterized as crystal with plane (110) at 2-θ equal to 27.3°, and by AFM test the roughness of films increased when the energy of laser increased too. The values of roughness between (6.77-13) nm, therefore the thicknesses increased to change from (34.88 - 165.48) nm, so the absorption of film increased because of the thickness of the film increased and we can get the optical energy gap between (3.6-3.9) eV.

Keyword: Titanium di-oxide, Thin films, Laser deposition.

تاثير غاز الاركون على الخصائص البصرية و التركيبية لاوكسيد التيتانيوم النانوي المحضر باستخدام طريقة الترسيب بالليزر النبضي

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الخلاصة:

يتناول البحث دراسة تاثير التغير في طاقة الليزر باستخدام غاز الاركون على بعض الخواص الفيزيائية لغشاء شبه موصل كااوكسيد التيتانيوم حيث تم استخدام ليزر الانديوم ياك النبضي بطاقات مختلفة تتراوح مابين (600–1000) ملي جول وبدرجة حرارة قاعدة 100 ^{0}م للقاعدة الزجاجية و تحت الفراغ بقدار يصل الى 10^{-3} ملي بار.

فحص حيود الاشعة السينية يبين ان الغشاء متعدد البلورات يظهر عند المستوي (110) عند زاوية حيود 27.3° و من خلال فحص AFM وجد ان خشونة السطح تزداد بزيادة طاقة الليزر و تتراوح ما بين (13– 6.77) نانومتر لذلك فان سمك الغشاء يزداد بشكل ملحوظ من (34.88–165.8) نانومتر وعليه فان قيم الامتصاص تزداد ايضا بسبب زيادة سمك الغشاء وايضا يمكن الحصول على قيمة فجوة الطاقة البصرية مابين (3.6–3.9) الكترون–فولت.

Introduction

Titanium dioxides (TiO_2) have attracted considerable interest due to their unique physical and chemical properties such as large energy gap, high refractive index,high dielectric constant, high optical transmittance in the visible and infrared spectral region and the absorption in the ultraviolet. The above properties make them useful for the optical applications as waveguides, and good stability in

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adverse environments [1-4]. Titanium oxide is widely investigated and employed as a functional material in a number of applications such as pigments, gas sensing, photovoltaics, photocatalytic and photo-electrochromic devices and self-cleaning surfaces [1, 5-7].

Titanium dioxide is a wide band gap semiconductor which exists in three crystallographic phases: rutile, anatase and brookite. The first two polymorphs have a tetragonal symmetry and due to their strong photocatalytic properties and stability have become materials of high scientific interest [8-10].

Rutile TiO_2 has some advantages over anatase phase, such as a higher refractive index, higher dielectric constant, higher electric resistance and higher chemical stability. Rutile TiO_2 has been traditionally used in pigment, plastic, construction and cosmetic fields because of its best light-scattering [11].

To date several chemical and physical techniques have been proposed to produce nanostructured titanium oxide: sol–gel, direct oxidation, electro-deposition, chemical vapor deposition (CVD) and physical vapour deposition (PVD). Among all PVD techniques pulsed laser deposition (PLD) has several unique features: a fine control on stoichiometry, the possibility to use thermally sensitive substrates (depositing at room temperature) and finally the capability to grow nanostructures and cluster-assembled films by ablating material in the presence of a background gas. In a gas, the expanding plasma plume experiences a spatial confinement due to increased collision rate of ablated species with the gas molecules thus favouring cluster formation [12, 13].

In the present work, preparation of nanostructure TiO_2 thin films using laser ablation, on heated glass substrates, in the presence of argon gas, still under vacuum was studied. Pulsed laser deposition (PLD) is a simple, low cost method to grow oxide films. Effects of film deposition conditions on the structural and optical properties of the films have been discussed.

Experimental Work

A high purity powder titanium oxide (99.999%) at 45° angle of incidence was compressed as a circular disk with 20 mm diameter and 3 mm thickness that used as a target. Films were deposited by PLD on cleaning glass substrates parallel to and 8 cm apart from the target. A pulsed Q-switched Nd: YAG laser with pulse duration 6 ns and wavelength (1064) nm with laser energies between (600-1000) mJ, and the target rotated with a frequency of 1 Hz. A typical set-up of PLD is schematically shown in the figure (1). All the films using Q-switched Nd:YAG laser with pulse duration 7 ns was focused through 120 mm focal length of converging lens. Figure (1) shows a typical set-up for PLD.

The target rotated with a frequency of 1 Hz and all the films were produced using 40 laser shots and deposited at a substrate temperature of 100°C (this growth temperature was optimum) in background gas argon with a pressure 200 mbar.

This Ar gas was let into the vacuum chamber through a needle valve. Surface roughness of the deposited films were observed by AFM (Shimatzu AA3000 Scanning Probe Microscope) and the crystal structure of the grown films was analyzed by the XRD system (Shimatzu 6000). Transmission spectra of the films were obtained by a UV- visible spectroscopy system (Shimatzu SP8001) double beam spectrophotometer.

Figure 1- The setup of PLD.

Results and Discussion

Optical Properties

The optical absorption of TiO_2 films on glass substrate prepared by PLD, were measured by UV-Vis spectrophotometer. From figure (2) it can be noticed that there are two regions, the absorption is very high in the wavelength (310 nm) and began decreasing until the wavelength (350 nm) and after this wavelength the absorption of the films become stable. The absorption of the films increased with increasing the energy of laser from (600 - 1000) mJ because the thickness of films increased with increasing the value of energy so the transmission decreased but the absorption increased.

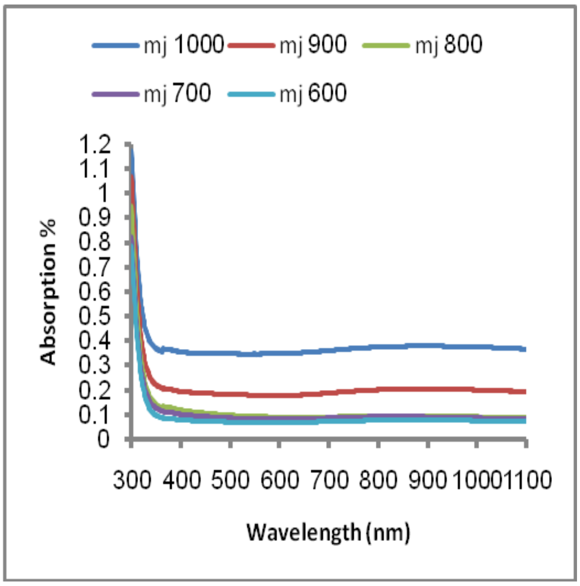

Figure 2- Absorption as a function of wavelength for different laser energies.

Figure -3 shows that the transmission is decreased with increased in laser energy due to increase the deposition efficiency and then the thickness of TiO_2 film. These values of transmission are about (40-85) % with laser energy (1000-600) mJ.

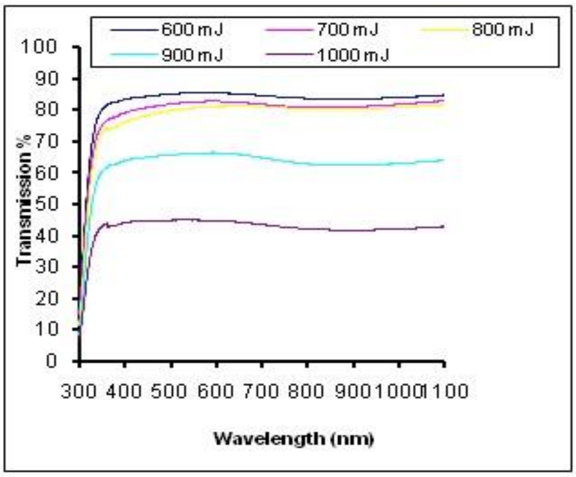

Figure 3- Transmission as a function of wavelength for different laser energies.

In figure (4) shows that, in case of using the argon gas the transmission will increase to reach 85% and the film's colors tend to whiteness, but when we did not use the argon gas the transmission reach to 60% and the color of the film was dark.

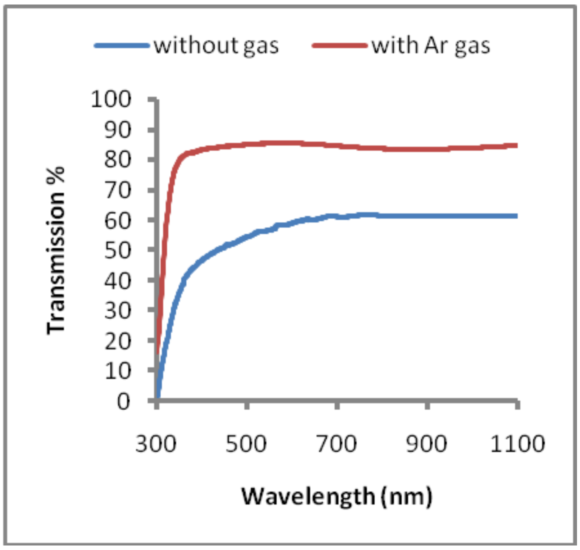

Figure 4- Transmission as a function of in the presence and absence of Ar gas.

Optical Energy gab

In order to determine the value of optical band gap energy (E_g) as well as the dominant absorption processes in TiO_2 material, the relation of $(\alpha h\nu)^2$ with the incident photon energy ($h\nu$) is explained in figure -5. The obtained value of E_g for TiO_2 films between (3.6-3.9) eV at different energy of laser, these values are higher than the bulk TiO_2. The relation was linear, which indicates that the TiO_2 obtained from this work has a direct energy gap and the direct allowed absorption processes are the dominant the energy band gap values increases with decreases laser energy see figure -5.

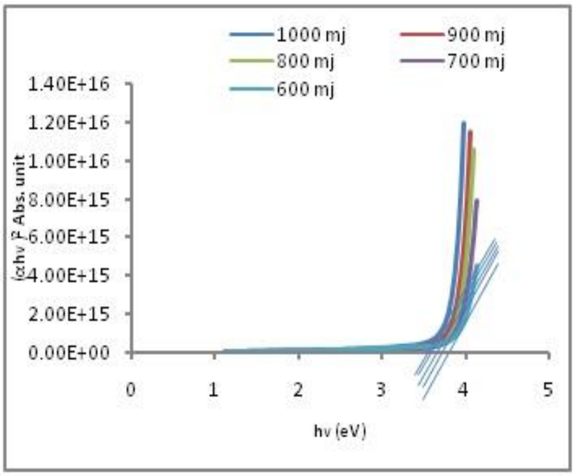

Figure 5- The relation between $(\alpha h\nu)^2$ and ($h\nu$) for TiO_2 thin films deposited at different laser energy.

Structure properties

1- X-ray diffraction

Figure 6(a,b) shows that, the X-ray diffraction patterns of TiO_2 thin films prepared at constant substrate temperature of 100 ˚C and at varying laser energy. In fgure 6(a) the film in the as depositd conditions have polycrystalline structure and the rutile phase have miller indicies (110) and (101) at diffraction angle 2θ=27.3˚ and 2θ=36.1˚ respectively. In figure 6 (b) we have shown the film is the single crystal structure and the TiO_2 has miller indicies, (110) at an angle 2θ=27.3˚[14-16].

It is clearly noticed that at laser energy (800 mJ), the film has high intensity in the rutile phase than that for the film deposited at laser energy (1000 mJ).From the XRD one can found that the grain size of the film at 800 mJ was (19.4 nm).

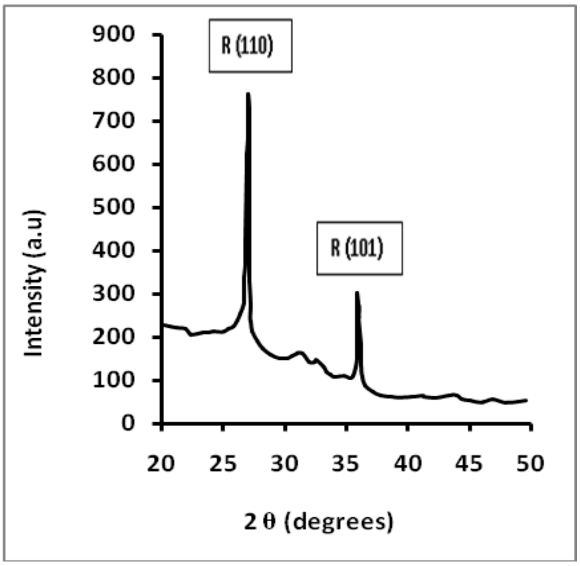

Figure 6 (a)- XRD of TiO_2 thin film at laser energy 800 mJ.

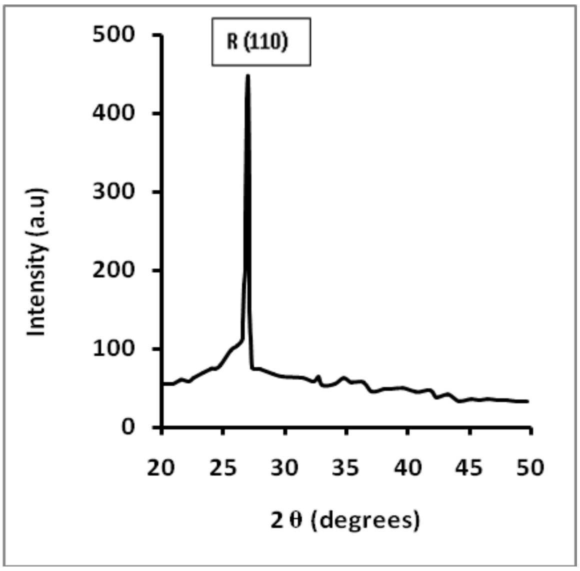

Figure 6 (b) - XRD of TiO_2 thin film at laser energy 1000 mJ.

2-Atomic Force Microscope (AFM)

Figure 7(a,b) gives the AFM topography images. The figure shows that with, the increase of laser energy, will increase the surface roughness, reaching (6.77,13) nm at laser energy (800, 1000) mJ respectively, laser energy 800 mJ one can see a homogeneous distribution for the nanoparticles as a result of an interaction between the molecules of TiO_2 and Ar gas, resulting nano-particles of TiO_2. We also note Effect of laser energy on the structural, morphology and optical properties of Nanocrystalline TiO_2 Thin Films Prepared by Pulsed Laser Deposition.

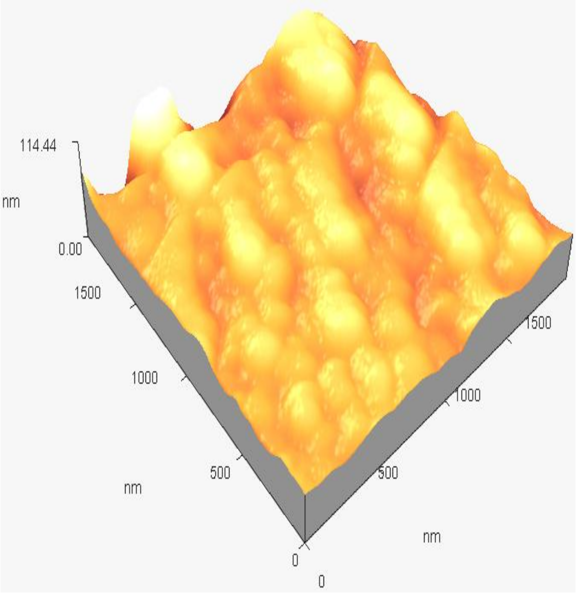

Figure 7 (a)- AFM image of TiO_2 thin film at laser energy 800 mJ.

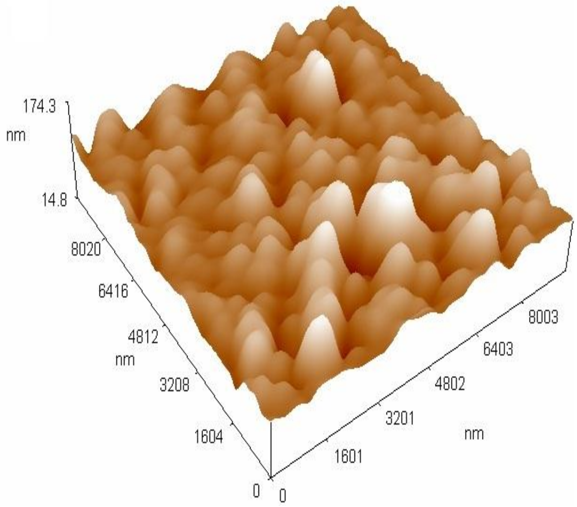

Figure 7 (b)- AFM image of TiO_2 thin film at laser energy 1000 mJ.

In the same time the thickness of film increased when increasing in laser energy led to increase the ablation process and the number of atoms that ablated from target therefore the thickness increased with laser energy as fig (8).

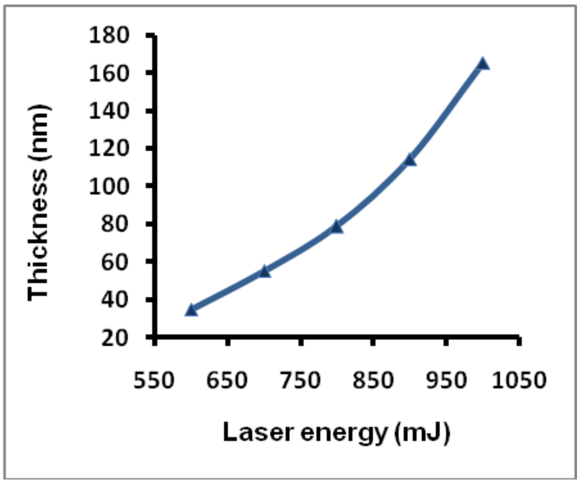

Figure 8- The effect of laser energy on the thickness for TiO_2 films.

Conclusion

From this research we were able to get nanostructure films by using pulse laser deposition technique at different laser energies. The structure, optical characteristics, and smooth surface morphology of the films as a function of laser energy had been investigated. The TiO_2 films in XRD test had plane (110) in rutile phase appeared the higher intensity of this peak at 800 mJ comparing with the results at 1000 mJ. The transmission increased with presence of argon gas and it decreased with increasing in laser energy also shoud be noted that the value of optical energy gap of films equal between (3.6-3.9) e.V by using pulse laser deposition technique.

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