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Influence of annealing time on structural, morphological properties of TiO_2 Films prepared by pulsed laser deposition

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المستخلص

تم تحضير اغشية من ثاني اوكسيد التياتينوم (TiO_2) بواسطة التبخير بنبضة الليزر وبمساعدة البلازما المتولدة على ارضيات من الزجاج. تم استخدام طيف حيود الاشعة السينية ومجهر القوة الذرية لدراسة الخصائص التركيبية والسطحية للاغشية الناتجة والتي اعطت معدل قطر جسيمات 43.10 nm. حيث لوحظ ازدياد ارتفاع شدة القمم في طيف الاشعة السينية مع زيادة زمن التلدين, بالاضافة الى ازدياد حجم الحبيبات. كما لوحظ تحسن مجمل الخصائص التركيبية مع ازدياد زمن التلدين. اظهرت قياسات مجهر القوة الذرية ان الخصائص السطحية للغشاء قد تحسنت مع ازدياد زمن التلدين. ويمكن ملاحظة تحضير اغشية ذات مواصفات جيدة جدا وتصلح للكثير من التطبيقات باستخدام البلازما المتولدة بواسطة الليزر متوسط القدرة.

Abstract

TiO_2 films were fabricated by pulsed laser deposition (PLD) on glass substrates. XRD and AFM were used to study structural and surface morphology. XRD chart revelled steady increments of the intensity of the main peak of TiO_2 of the films with the increase of laser power. The piratical sizes of the film were 43.10nm. The Atomic Force Microscope images show that surface roughness of the films was improved with the increase of laser energy. These results propose the possibility to enhance the structural properties of the TiO_2 films and also it is possible to obtain high quality TiO_2 film by variation of power laser.

Keywords: Nd-YAG LASER; structural properties; Surface roughness, TiO_2

Introduction

Due to the biological and chemical inert, titanium dioxide (TiO_2) represents the important inorganic solid yet. There are three phases of TiO_2 all of them are n-type, only anatase and rutile phases are

exploited for sundry technological applications[1]. The TiO_2 in film form has the suitable energy gap for many applications. This type of energy gap enhanced the electron transport by the photo potential separation. The corporation of TiO_2 with other materials has small gaps like CdS or metals introduces promising way for their use in chemical energy transformation [2-4]. TiO_2 layers are prepared by several techniques like chemical vapor deposition[5], sputtering, sol-gel[6, 7] chemical bathe deposition[8] and pulsed laser deposition (PLD)[9-11]. Among those techniques, PLD provides a simple process for unique contact film with excellent mechanical properties and high specific surface morphology and area. Both of Ti and TiO_2 used to fabricate TiO_2 thin film with lot of conditions (i.e. substrate type, type of gas and initial temperature) it make the difficult for comparing and recognize the differences in properties of the films in a consistent manner.

Deposition of TiO_2 by laser is a simple process yet, previously involves a complicated physical phenomenon, but now all are understood.

The aim of this work is to fabricate TiO_2 films by induced plasma from Nd: YAG laser at different power laser. Also calculate the structure and morphology parameters of the deposited TiO_2 via X-ray diffraction (XRD), and atomic force microscope (AFM).

Experimental

TiO_2 thin films were prepared by induced plasma from high power laser from Nd:YAG (1065nm) in 10 ns duration and total energy 70, mJ/cm^2 in an reaction chamber with a low pressure of 2.4 x10^{-4} torr. The diameter of Ti Sheet was 3.5cm and 99.9% purity which used as the target. Ti layer with thickness 1000 ± 2 nm were grown on glass substrates. the distance between Ti sheet and laser is 5 cm. Ti films were thermally treated for 1, 2, 3 and 4 hours at 450 °C in oxygen environment to transfer to TiO_2. The structural, morphological, and optical properties of the films was approved by using X-ray diffraction (XRD) type BRUKER's D8 ADVANCE (λ=1.5406 Å) at 2θ (20º-70º) and Atomic Forces Microscopy (AFM) type SEIKO SPI3800N.

Results and discussion

Fig.1 shows XRD spectra of TiO_2 film on glass substrate at different annealing time. The polycrystalline structure of TiO_2 appears in the XRD spectra . The position of peaks at 25.6, 38.4, 47.8, 55.1, 62.6 and 68.9, corresponding to (101), (112), (200), (211), (204) and (116) lattice planes, respectively. Furthermore, the XRD peaks approves the existence of one phase of TiO_2 anatase regarding to JCPDS

card 21-1272. The films samples are coded as 1, 2, 3 and 4 hours depends on the annealing time. It is very important to see that the nonappearance of any major shift in the peaks for all samples [12, 13]. It is possible to note that the anatase phase is favourable to the growth dynamics related with the mechanism of Ti^{+4}, O^{-2} ions connected in the structure to satisfy minimum free energy to the reaction on the grown surface or may be due to the high power of plasma induced at the surface which increase the kinetic energy of the ablated species impinging on the substrate at room temperature. The high peak (101) is chosen to calculate the particle size (D) using Scherrer formula [14]:

$$D = \frac{0.9\lambda}{\beta \cos(\theta)}$$

where λ is the wavelength,β is full width at half maximum (FWHM) and θ is the diffraction angle . The average particle size for samples at annealing time 1, 2,3 and 4 hours are 12.20, 13.48, 24.24 and 43.1 nm respectively. The grain size increment with increasing annealing time is attributed to the aggregate formation of particles with time.

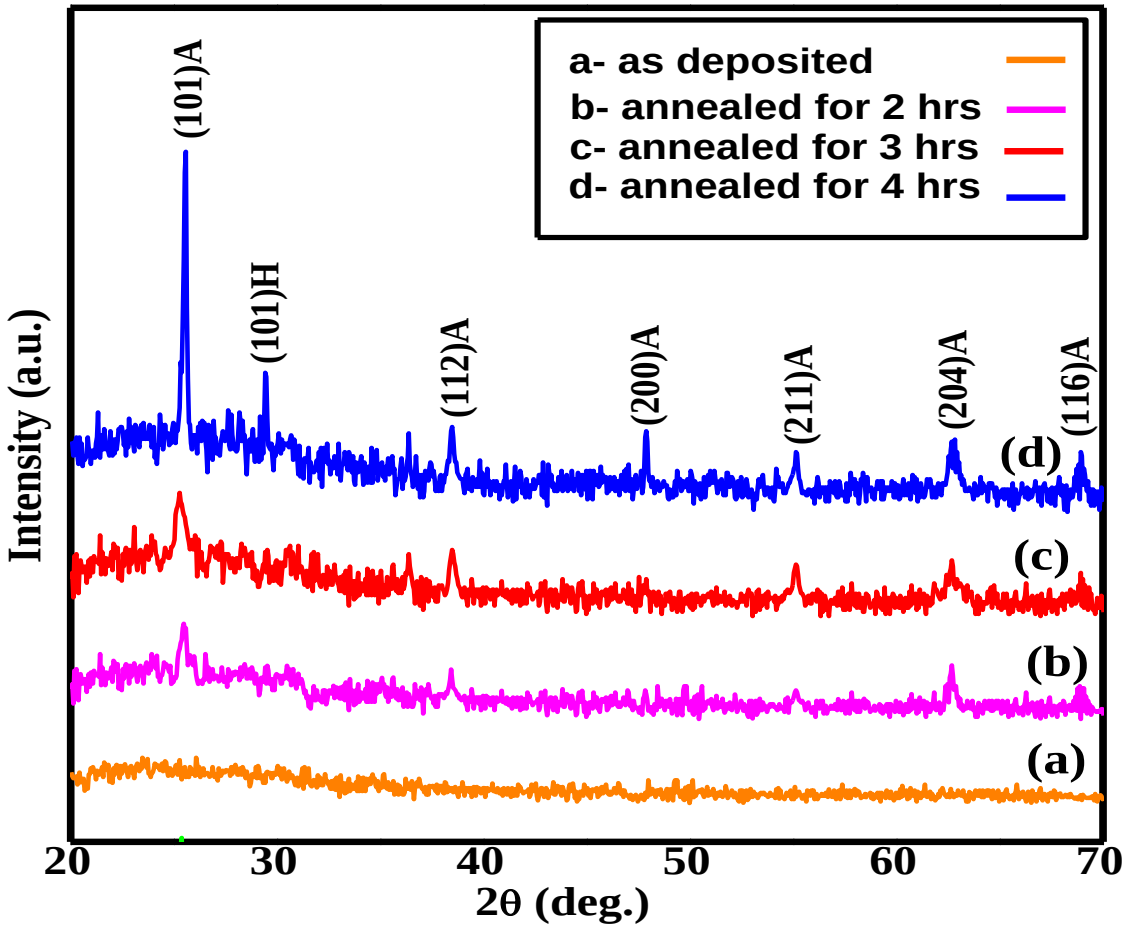

Fig.1 XRD patterns of TiO_2 film

The AFM measurement for the scanning area (1 μm × 1 μm) showing the surface morphology are illustrated in fig.2. Clearly shows AFM images that nanostructured nature of the films and the grain sizes were changed from nonmetric to sub-micrometric dimension with the variation annealing time. Fig.2 (a) represents the TiO_2 thin film showing smaller individual grains with low root-mean-square (R_{RMS}) roughness about 1.04nm. After annealing with oxygen shown in Fig.2 (b) displays substantial change in comparison to sample (a).

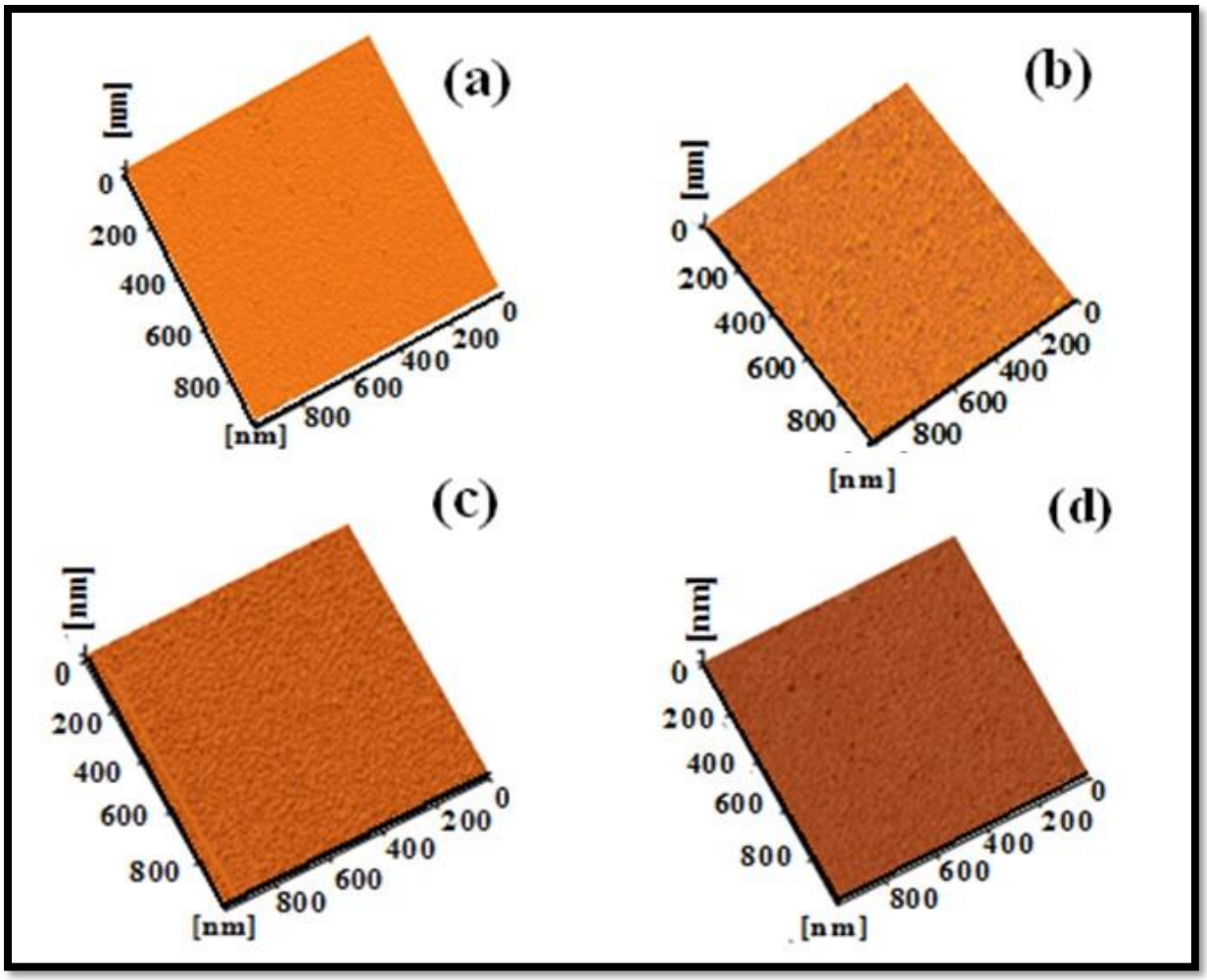

Fig.2 Atomic Force Microscope image of TiO_2 grown on glass surface (a) as deposited TiO_2 (b) annealing at 2 h (c) annealing at 3 h (d) annealing at 4 h

AFM images for samples (Fig.2 (c-d)) shows , it is clearly seen that in two samples the particles size increase by increasing time of annealed. The vertical height is tend to be larger than as deposited film value, indicating larger roughness and

increase the grain distribution with quite distance separation between grains especially for samples at 3 and 4 hours. This can be explained by the mean of the arrangement of corner - sharing TiO2. randomly arranged of corner- sharing octahedral may occur by increasing time of annealed. The observed large influence on the structural and topography is duo to the thermal process during and after deposition, which could enable migration of oxygen molecules through the TiO_2 film as reported. As can be seen from the surface topography, there is a preferred orientation of the regularly-shaped grains, which suggests the growth of the nanocrystalline of TiO_2 grains for all annealing temperature. However, TiO_2 exhibit higher porosity comparing with undoped films due to redistribution particle on the surface. Sample at 4h of annealing time presents the best surface quality to other samples optimal observed porosity and roughness. These results demonstrate that the laser ablation technique is an efficient method to produce a small size and narrow distributed of TiO_2 nanoparticles, which led to improve the surface properties of the film in presence heat treatment. However, our results suggest the possibility to carry out better crystallinity and higher activity in TiO_2 by controlling temperature.

Conclusion

TiO_2 films were deposited by pulsed laser deposition on glass substrates. Two steps method are used to produce film, deposition and thermal annealing. Variation of annealing time from 1 to 4 hours is applied to improve the structural properties. Nanostructured films comprised of nanocrystalline and nearly spherical nanoparticles was achieved. The very good features of the prepared HSF suggest that our method constitutes a basis for controlling the surface morphology and optical response in a tuneable fashion.

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