TiO_2 Thin Films on Si Substrate Obtained by PLD for Sensing Applications

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Abstract

Titanium dioxide (TiO_2) thin films were deposited by pulsed laser deposition on Si substrate. An KrF excimer laser with wavelength of 248 nm was used for the irradiation of TiO_2 targets. The substrates were heated during the film deposition at 400°C under an oxygen pressure of 35 mTorr, 50 mTorr and 65 mTorr. The XRD results reveal the growth of TiO_2 thin film deposited on Si substrate in pure anatase phase. AFM topography of as deposited film indicates the formation of uniform TiO_2 on substrate and particles size depending of the oxygen pressure. The optical properties of films have been recorded using UV-Vis spectrophotometer in the wavelength range 400-800 nm.

Introduction

TiO_2 thin films have been synthesized by using numerous methods including sol-gel [1], plasma oxidation [2], chemical vapor deposition (CVD) [3], metal organic chemical vapor deposition (MOCVD) [4], reactive magnetron sputtering [1], plasma-enhanced ALD (PEALD) and pulsed laser deposition (PLD) [5]. Among these techniques, PLD is one of the most promising techniques for the formation of complex oxide heterostructures, super-lattices, and well controlled interfaces at high melting points of oxide materials. This technique generally enables the deposition of highly dense films and has proven its efficiency in growing oxides of complex stoichiometry [6]. TiO_2 has been proven to be an effective material for applications such as photocatalysis [7, 8], dye sensitized solar cells [9], heterogeneous catalysis [10], self-cleaning surface coatings, sensors and anti-reflection coatings [5].TiO_2 thin film prepared by PLD has been studied by various research groups [10, 11]. However, different type of targets (*i.e.* Ti and TiO_2), variation in substrate materials, widerange of operation pressures, and the differences in synthesis temperatures make it difficult to compare and understand the differences in properties of the thin films [12]. TiO_2 is one of the most important semiconductors with high photocatalytic properties, stability, non-toxicity, wide band gap and high dielectric constant. TiO_2 can exist in three crystallographic phases: anatase, rutile and brookite. The dielectric constant of TiO_2 increases from amorphous to anatase and rutile phase [5]. The band gap of TiO_2 changes from 3.2 to 3.5 eV depending of crystalline phase. The anatase and rutile multiphase structures were observed in TiO_2 thin films by several researchers [13]. Variation in PLD deposition parameters such as oxygen pressure and target temperature results in the growing of TiO_2 thin films with different chemical and physical properties. It has been reported that the deposition of TiO_2 films on Si substrates at higher temperature leads to increase in oxygen vacancies as the surface Si atoms easily capture oxygen atom from TiO_2 [5].

In this paper, we report the successful growth of pure anatase phase TiO_2 thin films on Si substrate by PLD method. As TiO_2 target we used pure Ti foil, at fixed heated temperature 400°C and different conditions of oxygen pressures. Besides the composition and structure evolution as a function of oxygen pressure, we investigated the optical properties of the deposited thin films for further sensing applications.

Experimental

TiO_2 thin films were deposited on Si substrate by PLD technique using a NANO PLD-1000 system, PVD products. The KrF excimer laser Lambda Physik COMPex PRO 110 F with wavelength of 248 nm was used for deposition. The target used for ablation was commercial titanium foil with high purity (Aldrich, 99.97%). The target to substrate distance and deposition temperature was kept 75 mm and 400°C, respectively. To avoid major changes in the surface morphology of the target, which have negative effects on the deposition process, the substrates were rotated during the multiple laser irradiations with 10 rpm. The laser spot area on the Si surface was about 10 mm^2 and the laser pulse energy about 0.2 J. The laser beam incidence angle onto the target was chosen of 60°. Thus, the laser fluence onto the target surface was about $2J/cm^2$.

The irradiation chamber was previously evacuated down to a residual pressure of $8*10^{-6}$ Torr. High purity oxygen (99.99%) was then circulated inside the irradiation chamber through a calibrated gas inlet system. The oxygen pressure measured with an MKS controller was varying at 35 mTorr (TiO_2/Si-35), 50 mTorr (TiO_2/Si-50) and 65 mTorr (TiO_2/Si-65).The substrates were heated during the thin film deposition process at 400°C fixed temperature. Prior to introduction inside the deposition chamber, the Si substrates were carefully cleaned in ultrasonic bath in acetone, ethanol and distilled water for the removal of the impurities present on the surface. The films were annealed for 5 min after deposition.

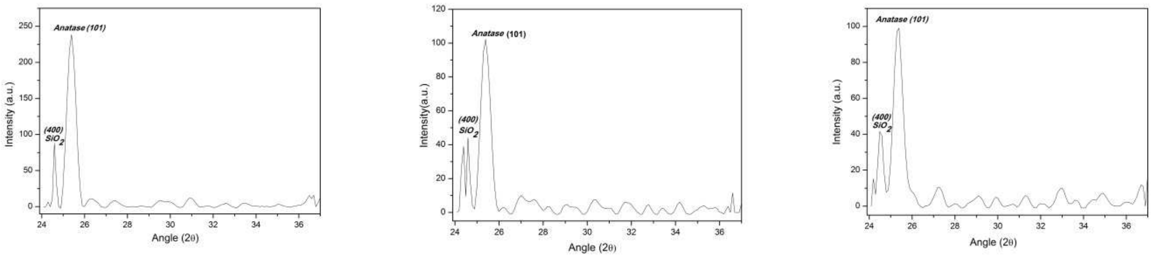
The surface morphologies of the deposited TiO_2 thin films were investigated by atomic force microscopy (AFM) using a Nanosurf® EasyScan 2 Advanced Research AFM apparatus. The crystalline phase of the deposited thin films was studied by X-ray diffraction (XRD) with a PANalytical X'PertPRO MPD Difractometer, Cu tube. The transmittance spectra for TiO_2 thin films on Si substrate annealed at 400°C were obtained in the range of 400-800 nm using the Lambda 950 Perkin Elmer UV-Vis spectrophotometer.

Results and discussion

TiO_2 thin films on Si substrate were characterized using XRD, AFM and UV-Vis spectroscopy. Influence of oxygen pressure on morphological and optical properties of TiO_2 thin films were discussed in detailed below.

X-ray diffraction analysis

X-ray diffraction of different TiO_2 thin films are shown in Fig.1. The spectra were recorded by using X-ray reflectivity module and the sample was aligned both to 2θ and ω angle. XRD pattern was recorded at $\omega = 4°$ and 2θ between 24° - 37° with a time per step about 200 s. For a better accuracy for each sample the analysis time was about 420 minutes. In the present study the diffractograms of all thin films deposited at different oxygen pressure (Fig.1 a-c) contain one intense line at 25.54° attributed to (101) lattice plane reflection of the tetragonal anatase TiO_2 phase indexed by Program XPert High Score-Plus (Ref. code 01-073-1764). It can be observed also the line at 24.56° attributed to (400) lattice plane assigned to SiO_2 indexed by Program XPert High Score-Plus (Ref. code 00-025-1332). Appeareance of SiO_2 peak in XRD pattern is probably because of highly oxidant medium and a heating temperature inside reaction chamber.

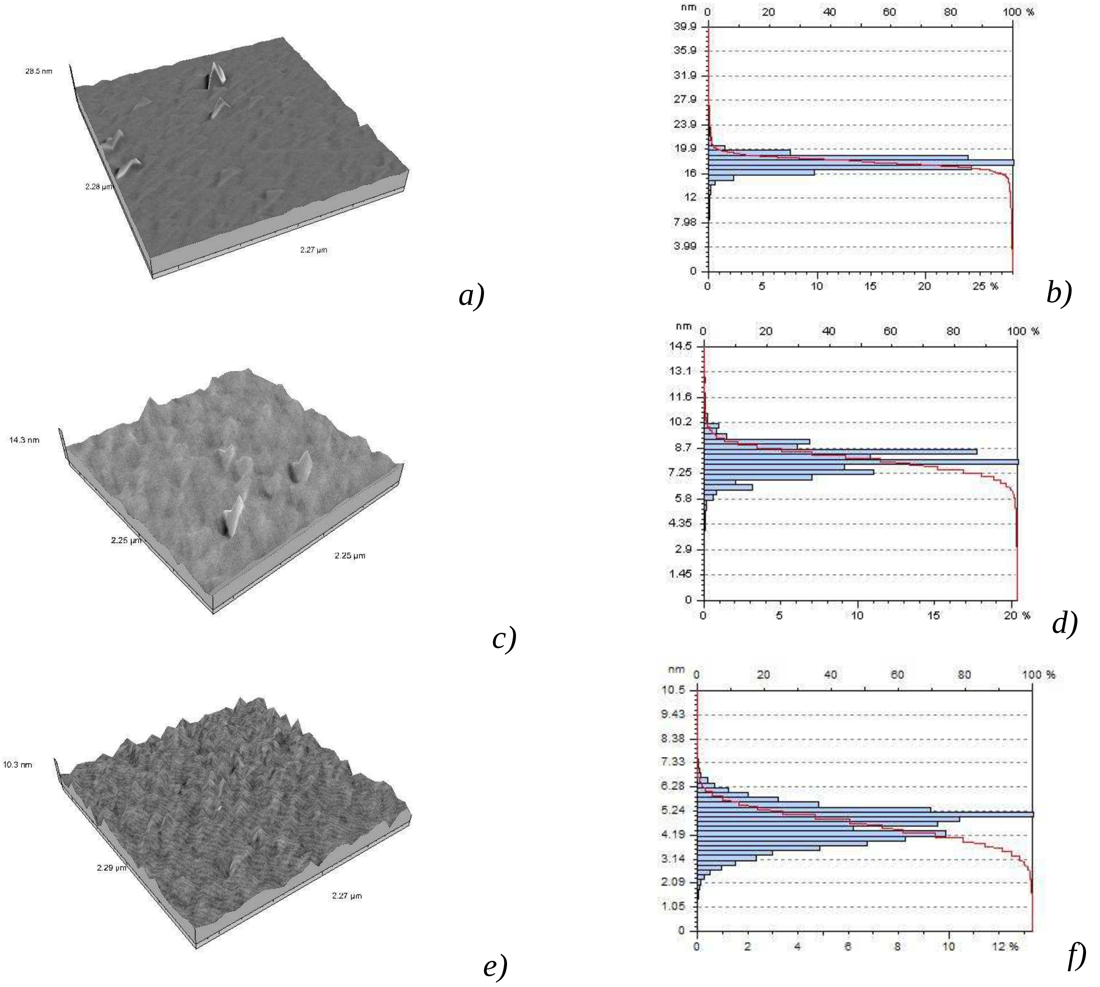


a) **b)** **c)**

Figure 1. XRD pattern of thin films TiO_2/Si-35(a), TiO_2/Si-50(b) and TiO_2/Si-65(c)

AFM microscopy

AFM images were recorded in the contact mode, at the scale of (2 x 2) μm^2. Figure 2 shows the 3D AFM images measured in deflection mode for deposited TiO_2 films on Si substrate. AFM images obtained in different areas of the films showed that the TiO_2/Si films reveal a homogenous nanostructure and a uniform deposition. Particle size analysis has been carried out on TiO_2 films surface using Nanosurf software by considering the image sizes of about 220 nm x 220 nm and the corresponding size distributions are shown in Fig. 2 b, c and f. The average nanostructure size obtained for TiO_2/Si-35 (Fig. 2b) is about 16 nm, and when the oxygen pressure increased at 50 mTorr (Fig. 2d) and respectively 65 mTorr (Fig. 2f) the particle sizes decreased at 5 nm.



a) *b)* *c)* *d)* *e)* *f)*

Figure 2. 3D AFM topography and particle size distribution of 2 µm x 2 µm scan area for TiO_2/Si-35 (a, b), TiO_2/Si-50 (c, d) and TiO_2/Si-65 (e, f)

Optical characteristics

The transmittance spectra in the wavelength range 400-800 nm of the TiO2 films are shown in Fig. 3. The transparency of the films lies between 25% and 35% in the spectra of the deposited films. The oscillations are absent in the optical spectra probably because the films are so thin (< 100 nm). The optical transmission of TiO_2 films in the visible wavelength region reduces with the increase of oxygen pressure indicating lower defect density near the band edge [15].

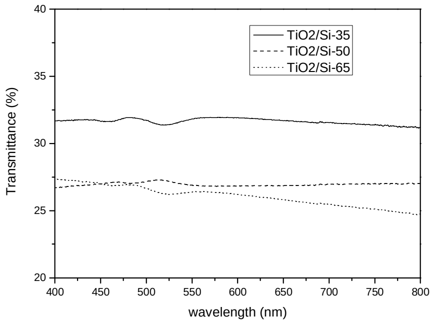


Figure 3. Optical transmittance of TiO_2 thin films

Conclusion

TiO_2 films have been deposited on Si substrate using PLD method in an oxygen atmosphere. The deposited films were characterized by XRD, AFM and UV-Vis techniques. XRD spectra suggested the formation of anatase TiO_2 independently of oxygen pressure. AFM topography of as deposited films indicates the uniformity of TiO_2 layer with an average size of 16 nm for a oxygen pressure of 35 mTorr, respectively 5 nm for 50 and 65 mTorr. The transparency in the visible range was found to be 35 % which fulfill the requirements of the sensing applications.

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