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PREPARATION OF TiO_X THIN FILMS BY REACTIVE PULSED-LASER ABLATION

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We report here on the characterisation of TiO_x thin films grown on glass and (100)Si substrates by reactive pulsed-laser ablation of a metallic Ti target. The specimens were prepared at two substrate temperatures (150 °C and 500 °C) under O_2 atmosphere with pressures ranging between 1 and 100 mTorr. The films grown at 150 °C change from a mixture of nano-crystalline suboxides dispersed in an amorphous Ti film (when p < 50 mTorr) towards a mixture of anatase TiO_2 nano-crystalline phase dispersed in an amorphous phase of Ti and its suboxides (when $p \geq 50$ mTorr). The films deposited at 500 °C mainly consist of a mixture of crystalline (101) TiO_2 anatase and amorphous phases. The films structure and composition are interpreted in terms of successive oxidation processes a) in the ablation spot; b) in the plasma plume, and c) during condensation at substrate site.

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1. Introduction

Various preparation techniques have been used to grow titanium oxide thin films [1-3]. Amorphous and rutile TiO_2 thin films have many applications in electronics, optics and medicine, while anatase TiO_2 became widely used as photo-catalytic materials [4]. Due to its superior flexibility and congruent evaporation, the pulsed-laser ablation (PLA) has focused the interest in both basic and applied research [4-8]. Little information is available at present concerning the use of the reactive pulsed-laser ablation (R-PLA) to grow TiO_x thin films. Sporadic theoretical and experimental approaches have been reported mainly concerning the investigation of gas-phase oxidation of Ti [9,10]. A full model of the R-PLA has not been developed yet to include all aspects of the reactions inside the plasma plume. The local-thermal-equilibrium model was used to describe the composition and the characteristics of the ablation plasma and predict the oxidation yields in the gas-phase [10]. To assess a general model, monitoring only ions/molecules may limit the full knowledge of the chemistry involved in reactive pulsed-laser deposition. Therefore, additional information from the characterization of R-PLA thin films is needed. Obviously, the general model will result in a better control of film properties. Results are given in this report on the use of R-PLA to grow TiO_x thin films under 1-100 mTorr O_2 atmosphere.

2. Experimental details

The TiO_x thin films were prepared in a high-vacuum chamber, which was evacuated to a base pressure of 1×10^{-6} Torr by means of a turbo-molecular pump. The details of the whole

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experimental setup are given in detail elsewhere [11]. The ablation of the Ti target (99.5% purity) was performed using 18000 laser shots (20 ns duration, 10 Hz repetition rate, 0.09 J/pulse) from a 248 nm KrF excimer laser (Lambda Physik COMPex 102). The laser beam, at the incident angle of 45°, was focused on a 3×1 mm^2 area of the ablated target. Due to optical losses in the system, an estimated fluence of 80 mJ/cm^2 was used, a value well below the splashing threshold of metallic Ti (10 J/cm^2) [5]. As previously reported [12] droplet-free Ti films could be routinely grown by us under pressure value as low as 10^{-4} mTorr using the same laser pulse shape, fluence values and set-up geometry. Prior each ablation process, the Ti oxides were removed from the surface of the target by 3 keV Ar^+ ion bombardment under base pressure conditions. The ablation spot was continuously swept over the target surface to ablate fresh material and diminish target exfoliation.

Before deposition, the substrates were cleaned-up in an ultrasonic bath in acetone, then rinsed and soaked in dry air. The specimens were grown on polished p-type (100)Si wafers and glass (Corning 7740 Pyrex® borosilicate) substrates placed at 2.5 cm in front of the Ti target, at low (150 °C) and high (500 °C) temperatures. Film morphology and composition were investigated by AFM, SEM and EDX spectroscopy. Cross-section SEM images of the films were used to evaluate film thickness with an estimated accuracy better than 5%. Information on film structure was inferred from XRD (Fe K_α radiation) and Raman (λ = 488 nm) data. The optical properties were assessed using transmittance data. The refractive index and optical absorption coefficient were calculated by transmittance envelope method [13]. Static contact angle measurements were performed using a home-made set-up.

3. Results and discussion

3.1. Film morphology and composition

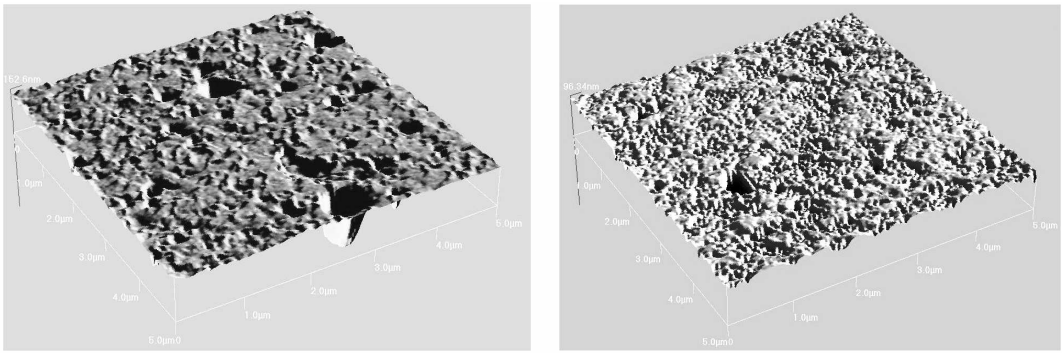
The thickness of the films under investigation ranges between 200 and 250 nm. Contact-mode AFM images show that the surface morphology changes significantly as an effect of O_2 pressure and substrate temperature (Fig. 1). Low oxygen content TiO_x thin films show a void rough surface, with no grain boundaries. A marked decrease in surface roughness is evident with increasing the O_2 pressure. For both 150 and 500 °C substrate temperature, the films deposited under 50 mTorr O_2 show a smoother surface with spike-like particulates. To evaluate the surface roughness of our films, the roughness coefficient, R_p, defined by the equation:

$$R_p = \frac{1}{D}\int_0^D |\, z_0 - z(x)\,|\, dx \tag{1}$$

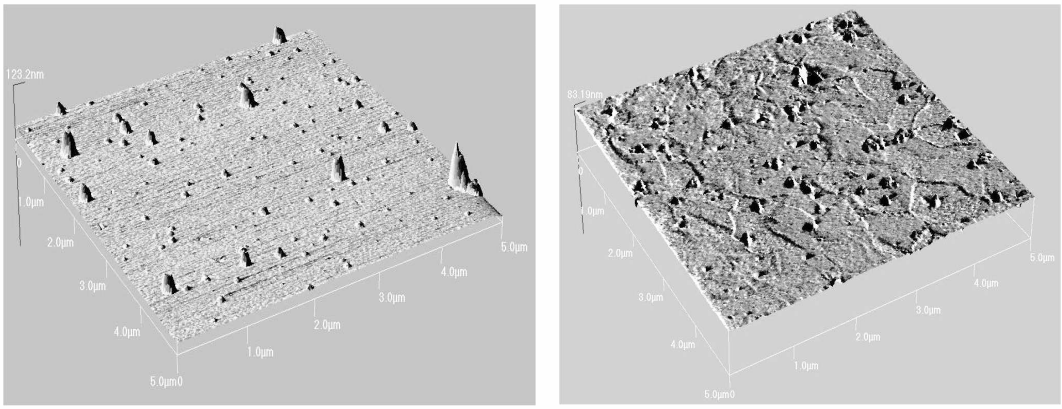
was evaluated over a surface of 3×3 μm^2. Here z_0 is average height over the interval from 0 to D along the x axis. It can be expressed as:

$$z_0 = \frac{1}{D}\int_0^D z(x)dx \tag{2}$$

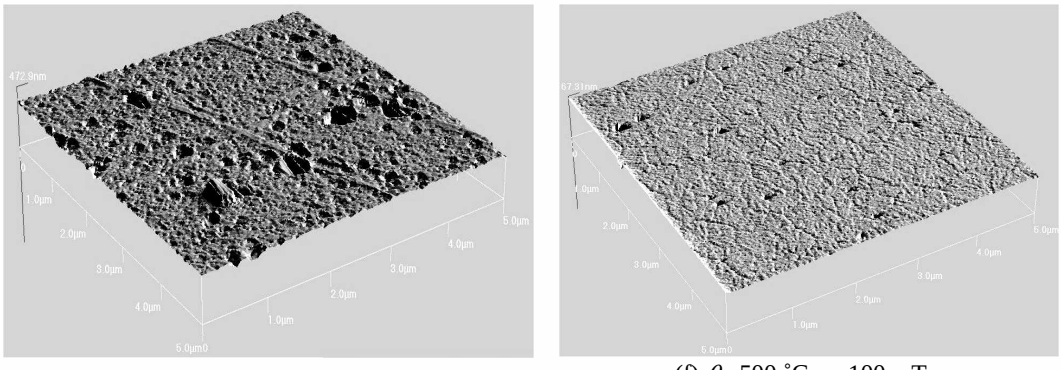
The roughness coefficient of the films decreases with 25% when O_2 pressure increases from 1 to 100 $\times 10^{-3}$ mTorr for both substrate temperatures. The films deposited at 500 °C under 50 and 100×10^{-3} mTorr O_2 show grain boundaries. They look more compact and voidless, a fact ascertained to an increased surface mobility of the condensing material during deposition.



(a) θ_s=150 ˚C, p= 1mTorr (b) θ_s=500 ˚C, p=1 mTorr



(c) θ_s =150 ˚C p=50 mTorr (d) θ_s=500 ˚C, p=50 mTorr



(e) θ_s=150 ˚C, p=100 mTorr (f) θ_s=500 ˚C, p=100 mTorr

Fig. 1. AFM images of samples grown on (100) Si substrates under 1, 50 and 100 mTorr O_2 at 150 ˚C and 500 ˚C.

The EDX spectra showed that the O/Ti atomic ratios in the films range between 1.40 and 2.12 when the O_2 oxygen pressure ranges between 1 and 100 mTorr (Fig. 2).

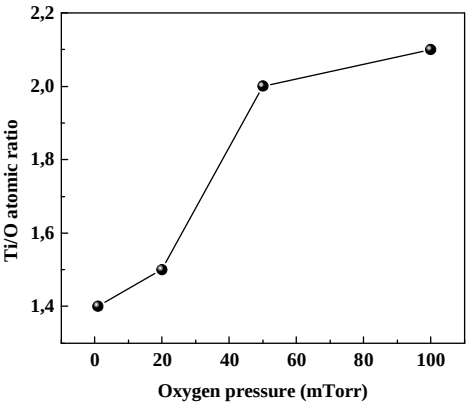


Fig. 2. Ti/O atomic ratio vs. O_2 pressure.

3.2. Film structure

The XRD patterns of the TiO_x thin films prepared by R-PLA (Fig. 3) are dependent on oxygen pressure and deposition temperature. XRD patterns show that the TiO_x films deposited at 150 °C are amorphous, irrespective of oxygen pressure. This is in agreement with previous data concerning preparation of TiO_2 films by standard pulsed-laser deposition of TiO_2 using titania targets, which show that as-deposited films on substrates below 500 ˚C do not show long-range crystalline ordering [11]. On the other hand, anatase and rutile diffraction peaks occur in the XRD patterns of the films deposited at 500 °C, and their area are function of O_2 pressure. As shown in Fig. 3, all the thin films deposited under O_2 increasing pressure from 1 to 100 × 10^{-3} mTorr O_2 display an increasing anatase (101) peak. A significant amount of rutile is present only in the films deposited under 1×10^{-3} mTorr O_2 pressure. No reflection from the (100) Ti plane was identified in the XRD plots.

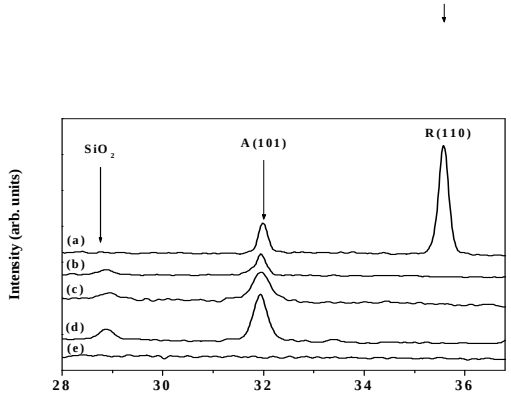


Fig. 3. XRD patterns of TiO_x films, for T_s =500 °C and: (a) $p(O_2)$ = 1 mTorr; (b) 20 mTorr; (c) 50 mTorr; (d) 100 mTorr. Curve (e) corresponds to a film grown at T_s=150 °C and $p(O_2)$ =100 mTorr.

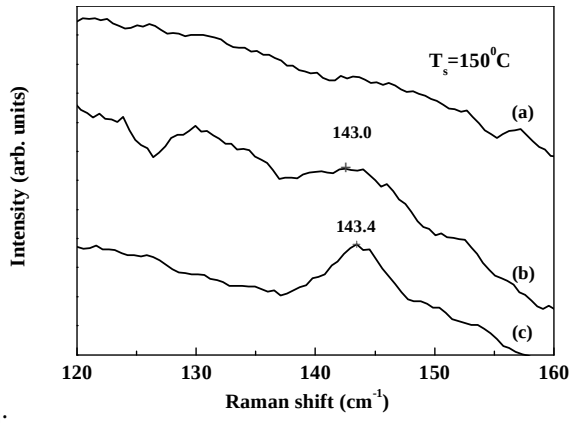


Fig. 4. Raman spectra of three TiO_x thin films deposited on Si at T_s=150 ˚C under $p(O_2)$ = 1, 50, and 100 mTorr (a, b, and c, respectively).

As is known, Raman can show local nano-scale crystalline ordering within domains with characteristic size of of 3-4 nm. In contrast to the XRD results, which indicated that all the TiO_x deposited at 150 °C look amorphous, Raman data show the E_{1g} mode peak at 144.4 cm^{-1}, which is specific for the anatase phase, in the film deposited under 100 mTorr O_2 and a smaller Raman peak for the film deposited under 50 mTorr O_2 (Fig. 4). As expected, Raman spectra of the films deposited at 500 °C show large Raman peaks within the entire O_2 pressure range. The peak height and FWHM

increase with the pressure, and a slight shift of the E_{1g} peak towards lower wavenumbers occurs, due to the decrease of oxygen vacancy concentration [9].

3.3. Optical properties

The optical transmittance spectra of the thin film deposited on the glass substrate at 500°C under an O_2 pressure of 100 mTorr show specific TiO_2 thin film features, with an UV absorption edge at 390 nm and a characteristic structure of maxima and minima due to optical interference in the transparent TiO_2 film. Their location allows for the calculation of the wavelength dependence of the refractive index, *n*, and the absorption coefficient, α, of the thin films. The values of the two parameters for wavelength between 300 and 1000 nm are listed in Table 1. The values of the refractive index are the same as for the anatase phase and with 13% lower than the high-index rutile [3].

Table 1. The values of the refractive index (*n*) and absorption coefficient (α) of a TiO_x thin film deposited at 500 °C by R-PLA under 100 mTorr O_2.

λ (nm)	300	400	500	600	700	800	900	1000
N	2.42	2.41	2.36	2.31	2.27	2.23	2.21	2.21
α (10^3 cm^{-1})	828	594	259	258	247	246	242	229

For the sample deposited at 500 °C and 100 mTorr O_2, the contact angle of water with the film decreased from 86° to 12° after irradiation with 3J of (non-focused) UV radiation from the same excimer laser, normally used for laser ablation. The contact angle recovers to the initial value after 72 hrs. Higher saturation value of the contact angle (19°) and shorter recovery time (4 h) were observed for the film deposited under 20 mTorr O_2. Long-term recovery of the contact angle is a strong evidence of the photocatalytic activity of the film.

TiO_x film structure and composition can be interpreted in terms of successive oxidation processes: (a) in the ablation spot; (b) in the plasma plume, and (c) during condensation at substrate site. To our best knowledge, little information is available now in the literature on the oxidation reaction rate of Ti at the target site, as an effect of laser ablation. It is expected that a heating-enhanced oxidation process takes place in the ablation crater, where temperature values of several hundreds of degrees are currently reached. In our experiments fluence conditions have been kept constant, therefore the current data can be interpreted in terms of the kinetics of the occurrence of the Ti-O bonds both in the gas phase and at substrate site.

The formation of Ti-O bond in the gas phase is exothermic, with a binding energy of 6.98 eV and a reactive cross-section of 22.6 $Å^2$ [9]. It was found that $Ti\text{-}O^+$ molecular ion occurs in the ablation gas plasma under O_2 pressures as low as 10^{-6} Torr. On the other hand, low-energy ion scattering data [14] showed that the topmost layer of the Ti surface exposed to low-pressure O_2 atmosphere reaches oxidation saturation after a characteristic time of the order of 100 s, under an O_2 pressure of 10^{-8} Torr. The oxidation rate increases rapidly with temperature, both in the gas phase and at the substrate site with temperature, as EDX spectra showed for the TiO_x films. A further decrease of oxygen vacancy concentration can be achieved by post-deposition oxidation of the films in O_2 atmosphere [11].

4. Conclusion

Titanium oxide thin films have been prepared by reactive laser ablation of a Ti target under oxygen atmosphere. Our XRD and Raman data show that a significant amount of anatase TiO_2 is

present in our films. The TiO_x thin films show increasing oxygen content when the O_2 gas pressure during R-PLA increased from 1 to 100 mTorr. TiO_x films feature increasing crystallinity with substrate temperature and O_2 pressure. The thin films deposited at 500 °C at under 100 mTorr O_2 are essentially anatase TiO_2. This conclusion is further sustained by the values of the energy gap and recovery time of the contact angle of the films with water, which are very close to the PLD TiO_2 films prepared by us using TiO_2 ceramic targets [11]. Further XPS measurements are now in progress to quantify the O/Ti atomic ratio both in the surface region and in deeper layers of the TiO_x films.

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