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Effect of annealing and O_2 pressure on structural and optical properties of pulsed laser deposited TiO_2 thin films

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ABSTRACT

In this paper, effect of annealing and O_2 pressure on the structural and optical properties of pulsed laser deposited thin films of TiO_2 is reported. XRD, FTIR spectra and SEM images confirm that at high annealing temperatures, the rutile phase and crystalline quality of thin films increases. Higher pressure of O_2 during deposition improves the rutile phase and favors the rod like growth of TiO_2 thin film. The red shift in photoluminescence (PL) spectra of TiO_2 thin films with annealing temperature is reported. Contact angle measurement data for the thin films reveals the hydrophobic nature of the films. The very low reflectivity (∼10%) reported in this paper may be promising for anti-reflection coating applications of pulsed laser deposited TiO_2 thin films.

1. Introduction

TiO_2 is an important n-type wide band gap II–VI semiconductor with high refractive index and high dielectric constant. TiO_2 thin films have drawn a great deal of attention in recent years due to their wide application in solar cells, photo catalyst and self cleaning windows [1–3]. TiO_2 thin films have found applications in multilayer optical filter [4], anti-reflection coating [5] and metal–insulator–semiconductor (MIS) devices [6]. Room temperature grown TiO_2 thin films can have three structural forms anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Annealing at temperatures between 300 °C and 800 °C initiates a transition from primary anatase to the rutile phase [7,8].

Deposition of TiO_2 in anatase as well as rutile phase has been reported very well in the literature [5,7,9]. Among all the reported techniques, pulsed laser deposition (PLD) provides the precise manipulation of the properties of thin films of TiO_2 by controlling the deposition parameters [9–14]. Normally, TiO_2 thin films deposited at room temperature are amorphous with the anatase phase which gets converted to rutile phase after annealing [15] as former being thermodynamically unstable. Ambient oxygen pressure and post-deposition annealing are the most important parameters that affect the phase formation, morphology and microstructures and optical properties of pulsed laser deposited TiO_2 thin films. Xin et al. [16] discussed the effect of oxygen pressure on the structural properties of Co-doped TiO_2 films and Long et al. [17] have reported effect of substrate temperature and ambient pressure on the microstructure of TiO_2 films. However, the effect of ambient pressure and post-annealing is not well documented in the literature for room temperature deposited TiO_2 thin films using PLD.

In the present paper, we have reported pulsed laser deposition of high quality TiO_2 thin films at room temperature in oxygen ambient using high purity TiO_2 pellet. The effect of ambient pressure (O_2) and post-deposition annealing over structural, optical properties and the contact angle with water of pulsed laser deposited TiO_2 thin films is presented.

2. Experimental setup

The experimental setup used to deposit the TiO_2 thin films is shown in Fig. 1. The second harmonic of Q switched Nd:YAG laser (Model—Quanta systems-HYL101, 400 mJ/pulse in fundamental with 8 ns pulse duration and 10 Hz repetition rate) is focused on to the rutile TiO_2 of high purity (sintered at 1100 °C for 3 h and at 1200 °C for 18 h) target with a lens of focal length of 35 cm. The target was mounted inside the vacuum chamber through a motorized vacuum feed through and continuously moved in order to avoid piercing with the repeated shots of laser. The chamber was initially evacuated to a base pressure of 10^{-6} mbar and then filled with O_2 gas in the pressure range of 10^{-1} mbar to 10^{-3} mbar. When the high power laser was focused on to the TiO_2 target in the ambient of O_2 gas, plasma containing neutral

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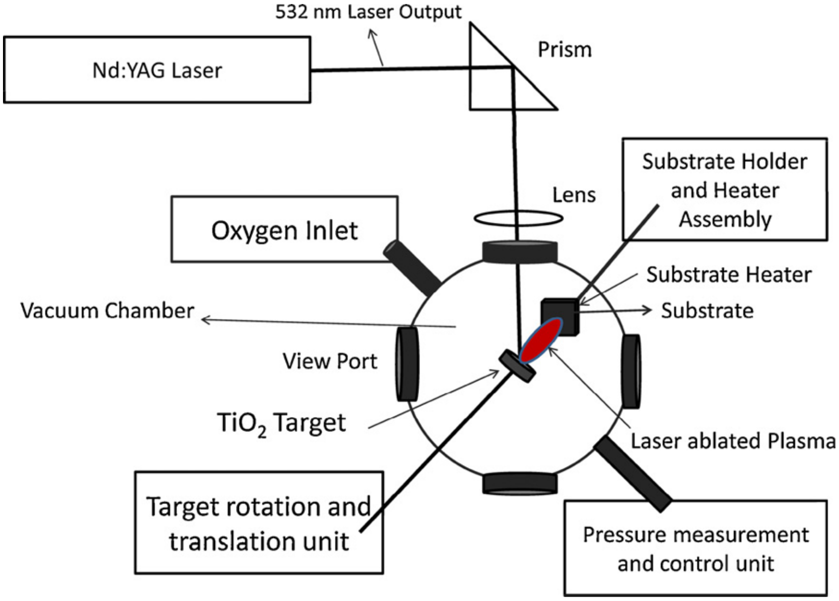

Fig. 1. Experimental setup.

and excited species of titanium and oxygen expanded and undergoes through the proper dynamics and finally thin films of TiO_2 were deposited on ultra sonically cleaned, polished glass substrates placed parallel to and 3 cm apart from the target at room temperature as shown in Fig. 1. Deposition time was kept fixed for 30 min for all the results reported in this paper. After deposition, TiO_2 thin films were annealed in high temperature furnace for 6 h at different temperatures in the range of 400–650 °C in air. These films of TiO_2 were scanned with SEM (LEO-1430vp) for surface morphology and XRD (SEIFERT 3003) for the crystal structure. Optical characterizations were performed with UV–vis spectrophotometer (Cary 100 Varian), photoluminescence (Thermo-spectronic Aminco Bowman Series 2) and FTIR (Horriba Jobin Yuvon). Contact angle measurement of TiO_2 films annealed at different temperature was performed by the pendant drop technique using Phoenix

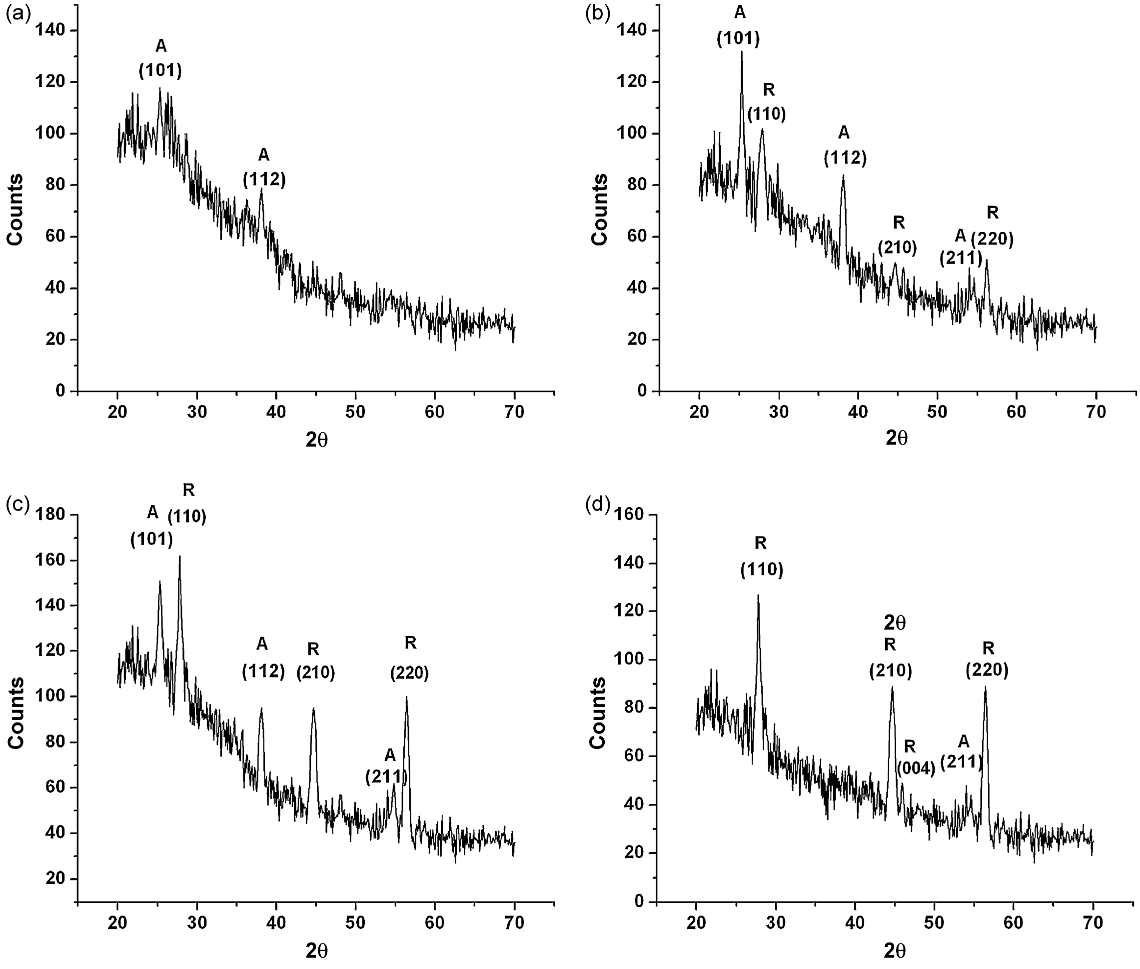

Fig. 2. XRD pattern for TiO_2 thin films deposited at 10^{-1} mbar O_2 pressure at room temperature; post-annealed at (a) as-deposited (b) 400 °C (c) 500 °C and (d) 650 °C.

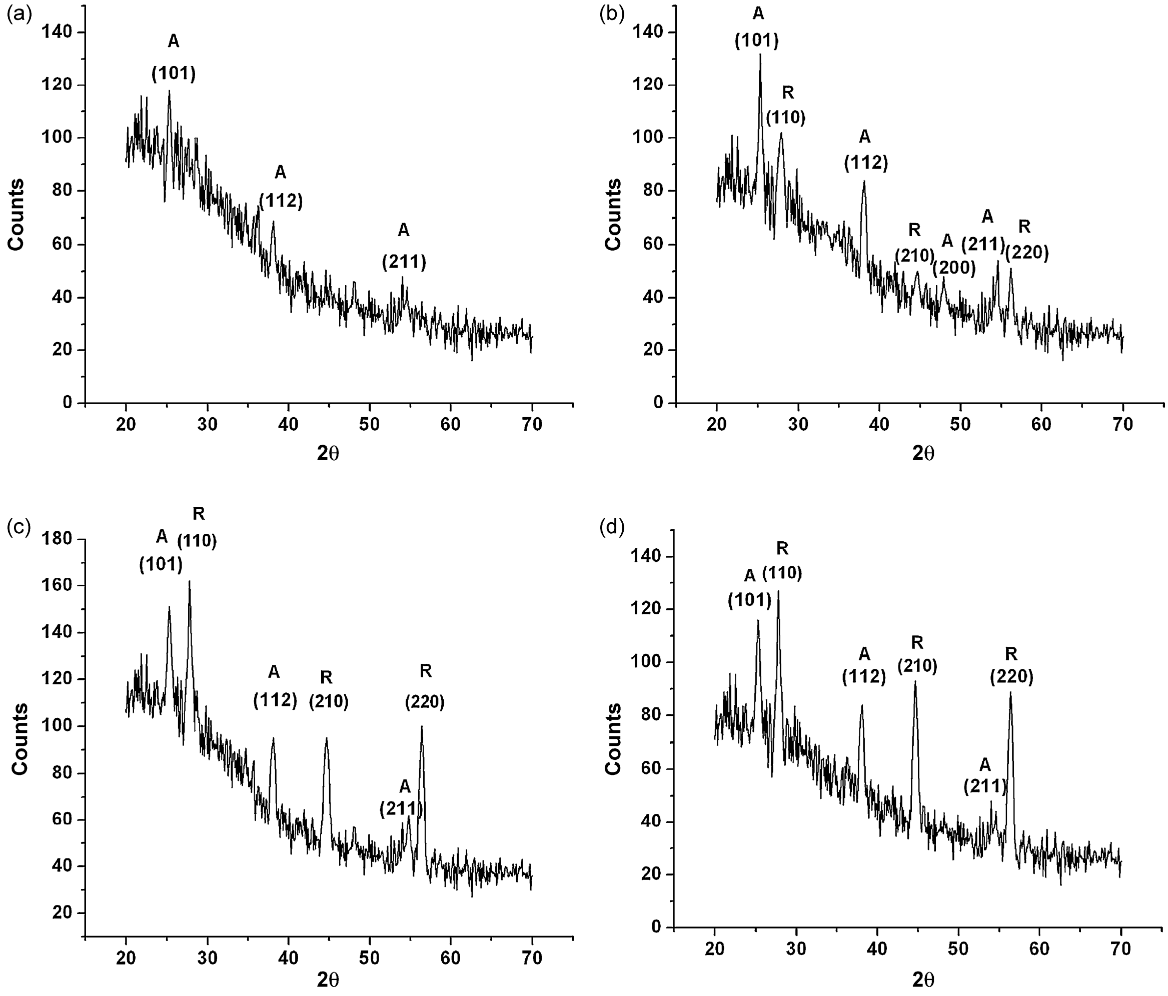

Fig. 3. XRD pattern for 500 °C post-annealed TiO_2 thin films deposited at different O_2 pressure at room temperature: (a) 10^{-3} mbar (b) 10^{-2} mbar (c) 10^{-1} mbar (d) 1 mbar.

150/300 ac contact angle analyzer. Deionized water was dispersed onto the specimen by dropping from the SS needle onto the thin film surface and from the tangent, contact angle was measured.

3. Results and discussion

3.1. Structural properties

Fig. 2 shows XRD pattern for PLD grown TiO_2 thin films deposited on glass substrate at room temperature at 10^{-1} mbar O_2 ambient with different annealing temperatures. In Fig. 2(a), it is clearly visible that as-deposited TiO_2 thin films showed amorphous nature with anatase phase. Crystalline nature of the films was improved with annealing temperature and at 400 °C and above, rutile phase started appearing as shown in Fig. 2(b). With further increase in temperature, rutile phase started dominating (Fig. 2(c)) and at 650 °C almost complete phase transition takes place from anatase to rutile. Fig. 3 shows XRD patterns of post-annealed (at 650 °C) TiO_2 thin films deposited at room temperature at different pressures of O_2 ambient. It is clear from the XRD patterns that the TiO_2 films deposited at high O_2 pressure (>10^{-1} mbar) have better crystalline quality compared to films deposited at lower O_2 pressure (<10^{-2} mbar) and rutile phase dominated at high O_2 pressures.

3.2. Surface morphology

Fig. 4 shows SEM images of pre- and post-annealed (at 650 °C) TiO_2 thin films deposited at room temperature at 10^{-1} mbar O_2 ambient. Surface morphology of as-deposited TiO_2 thin film was amorphous like while post-annealing changed the surface morphology into tubular shaped crystalline structures.

Fig. 5(a) and (b) shows SEM images of post-annealed at 650 °C TiO_2 thin films deposited at two different O_2 ambient pressures (10^{-3} mbar and 1 mbar respectively). High O_2 pressure favors the rod like surface morphology of crystalline TiO_2 thin films (Fig. 5(b)). Fig. 5(c) shows high resolution SEM image of TiO_2 nanorods arranged in flower like pattern, deposited at 1 mbar O_2 pressure. There was not much change in film composition with increasing oxygen pressure as shown by EDAX spectra of the TiO_2 thin films (inset). Elemental analysis was carried out for Ti and O and average atomic percentage was found to be 33.2:66.8 (Ti:O) showing good stochiometric ratio. Fig. 6(a) and (b) shows cross-sectional SEM images of room temperature deposited TiO_2 thin films at 10^{-2} mbar and 1 mbar respectively. The film thickness is increased from 1340 nm to 2150 nm with increase in O_2 pressure from 10^{-2} mbar to 1 mbar as density of TiO_2 plasma propagating towards substrate is higher during PLD at higher O_2 pressures. This also gives rise to more and more nucleation centers available for the transformation into rutile phase upon annealing [8]. At low O_2 pressure, the bombardment of deposited particles on to the substrate takes place at higher energy which may spoil the lattice structure making the film more amorphous in nature. Post-annealed TiO_2 films were highly stable in nature and even after six months of deposition, no degradation of film quality was observed. The anatase phase is thermodynamically less stable and post-annealed film undergoes a phase

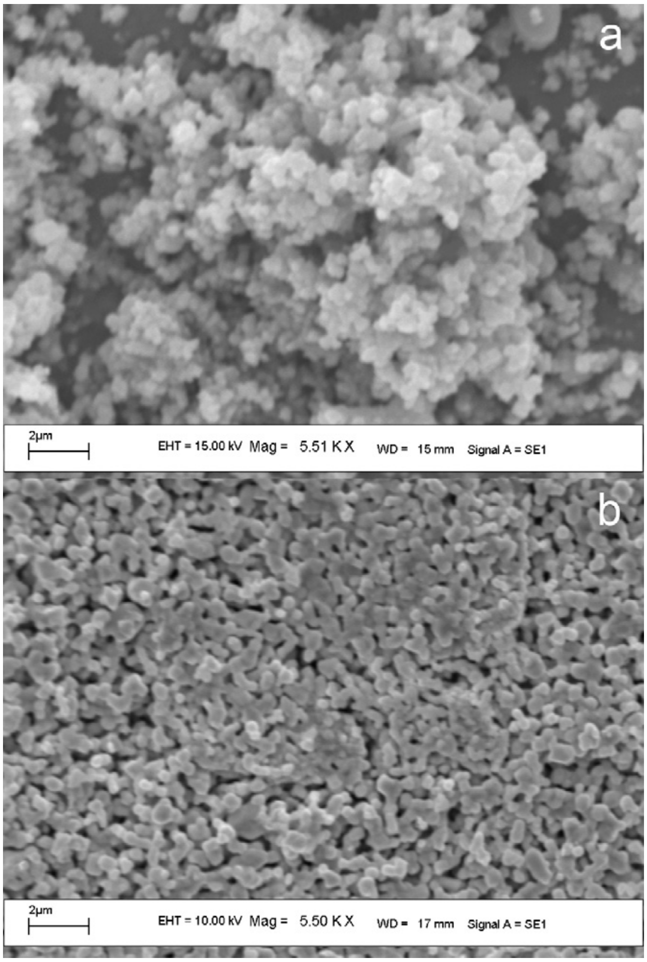

Fig. 4. SEM image and EDX spectra of room temperature deposited TiO_2 thin films at 10^{-1} mbar O_2 pressure: (a) as-deposited, (b) annealed at 650 °C.

transformation to rutile phase which is very stable in nature [15].

3.3. Optical properties

Fig. 7 shows the transmittance spectra in ultraviolet and visible region of TiO_2 thin films deposited at 10^{-1} mbar O_2 pressure, annealed at different temperatures. The transmission of TiO_2 thin films decreases with the increase in annealing temperature. The absorption edge for unannealed TiO_2 film (curve A of Fig. 7) was observed at 380 nm [7]. When TiO_2 film is annealed under lower temperature ($T \sim 500\,^{\circ}C$), the transmittance of the TiO_2 films decreased slightly. In visible region, the average transmittance of TiO_2 film annealed at 500 °C was ~70%. When the annealing temperature is raised to 650 °C, the transmittance of TiO_2 film further decreased to ~50% and a red shift in absorption edge was observed. This further confirms formation of rutile phase at higher annealing temperatures in accordance with the XRD results (Fig. 2).

A separate UV–vis spectrophotometer with an integrating sphere was used to record UV–vis diffuse reflectance spectra (DRS). Fig. 8 shows the diffuse reflectance spectra in UV–vis region of annealed TiO_2 thin films. It can be seen that reflectance of TiO_2 thin films increases with increase in annealing temperature. Room temperature deposited TiO_2 thin films (unannealed) at 0.1 mbar O_2 ambient showed only about 10% reflectance, which can be very useful for anti-reflection coating applications. For films annealed at temperatures as high as 650 °C, reflectance increases up to 20%.

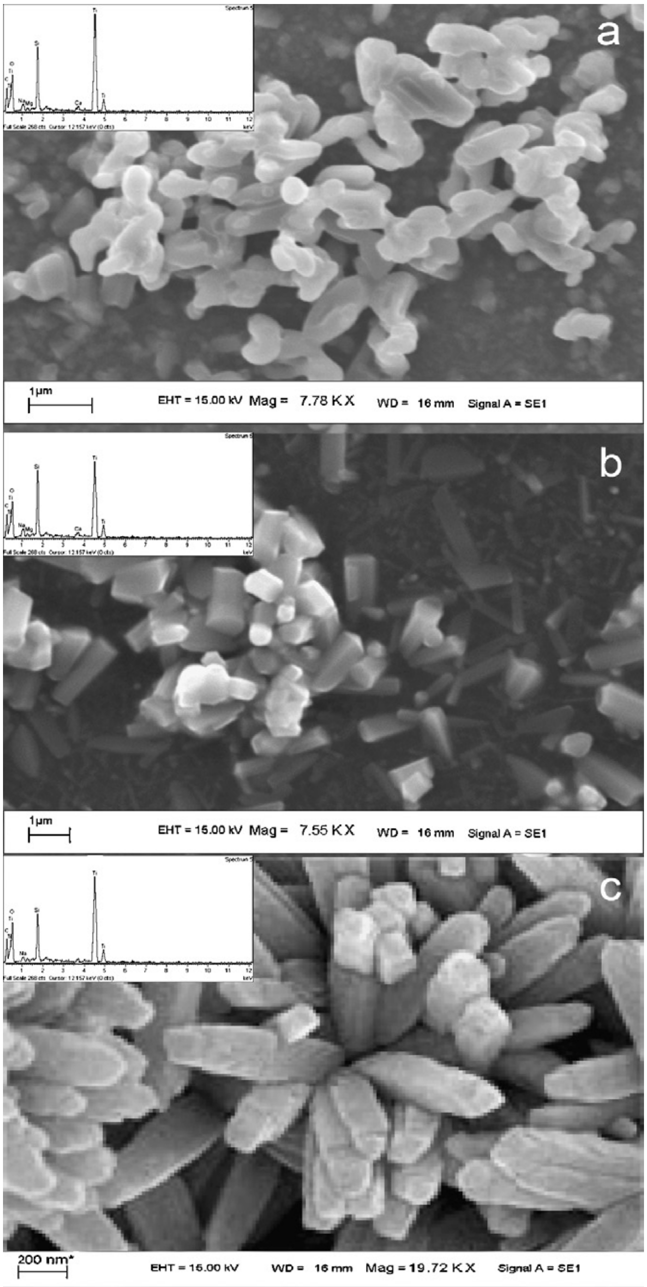

Fig. 5. SEM image and EDX spectra of 650 °C post-annealed TiO_2 thin films deposited at (a) 10^{-3} mbar O_2, (b) 1 mbar O_2 pressure and (c) 1 mbar O_2 pressure (high resolution image).

Fig. 9 shows photoluminescence (PL) spectra of TiO_2 thin films. The PL is found to increase slightly with increase in annealing temperature as crystalline structure of deposited films improves. A large red shift in PL from 396 nm to 415 nm is observed in annealed thin films due to the formation of rutile phase which has band gap of about 3.03 eV while anatase TiO_2 has band gap of about 3.26 eV [18,19].

Fig. 10 compares the PL spectra of TiO_2 thin films deposited at different O_2 pressures, annealed at 500 °C. The PL of TiO_2 thin films increased with O_2 pressure. This behavior is attributed to the increase in thickness (Fig. 6(a) and (b)) and crystalline quality of TiO_2 thin films at high O_2 pressures.

The contact angles between water drop and TiO_2 film surface, measured by drop shape analysis, were found to increase from 36° to 65° with increase in the annealing temperature. This shows

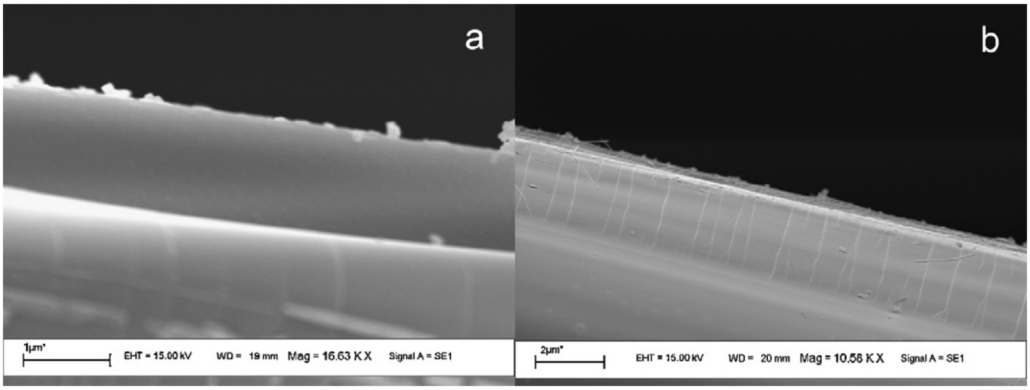

Fig. 6. Cross sectional SEM image of TiO_2 thin films: (a) 10^{-2} mbar O_2, (b) 1 mbar O_2 pressure.

that the films are fairly hydrophobic in nature and tend towards more hydrophobic in nature after annealing. Hydrophilicity and hydrophobicity of the TiO_2 film have been reported to have relationship with the stoichiometry. It has been reported that anatase phase shows the lower angle and thus higher hydrophilicity [20]. Table 1 lists the contact angle between water and typical TiO_2 thin film surface deposited at 10^{-1} mbar O_2 pressure at room temperature followed by post-annealing at different temperatures.

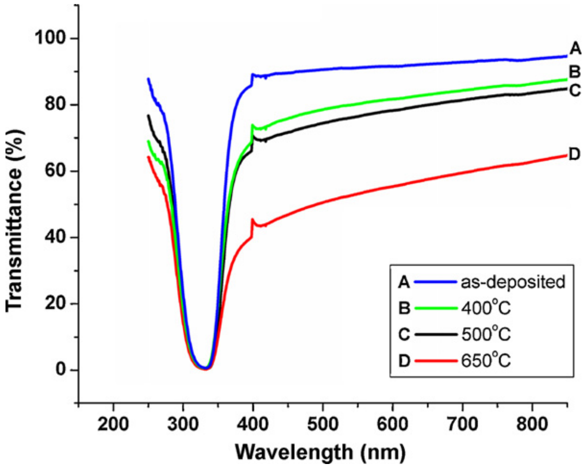

Fig. 7. Transmission spectra of as-deposited and annealed TiO_2 thin films.

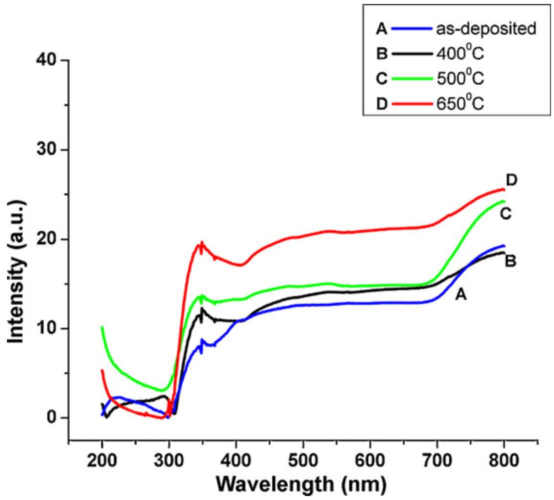

Fig. 8. Diffuse reflectance spectra of as-deposited and annealed TiO_2 thin films.

Fig. 11 shows FTIR spectra of pulsed laser deposited TiO_2 thin films at different annealing temperatures. FTIR spectra further confirmed formation of mixed anatase–rutile TiO_2 phase at higher temperatures. The peak at 448 cm^{-1} was attributed to anatase TiO_2 phase and denoted by A-TiO_2. The peaks at 423 cm^{-1}, 608 cm^{-1},

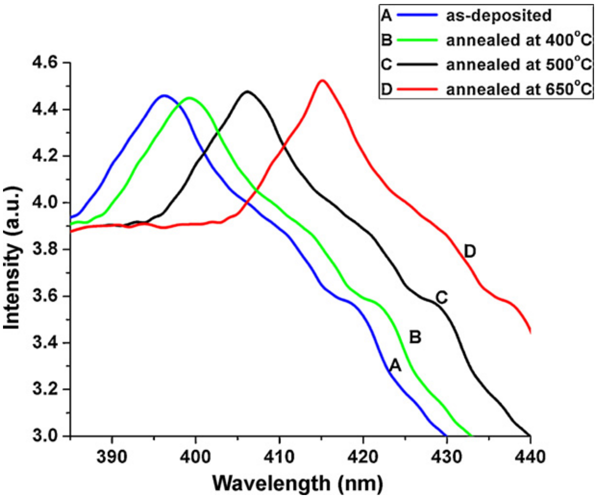

Fig. 9. PL spectra of as-deposited and annealed TiO_2 thin films.

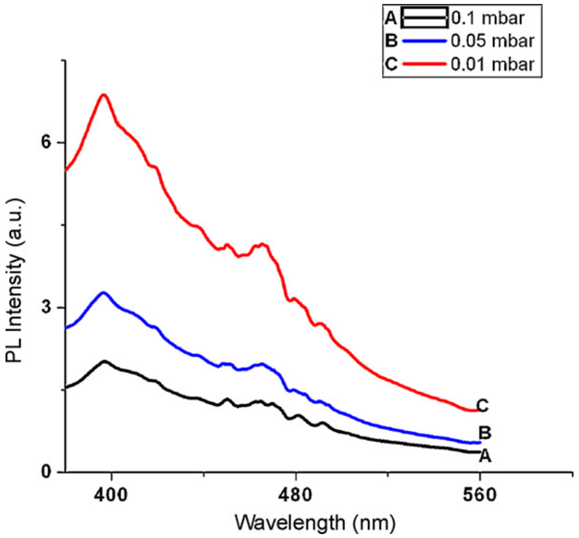

Fig. 10. PL spectra of 500 °C annealed TiO_2 thin films deposited at different O_2 pressures.

Table 1
Variation of contact angle of TiO_2 with water for different annealing temperatures.

Annealing temperature (°C)	Contact angle (°)
As-deposited	36
300	56
450	60
500	65

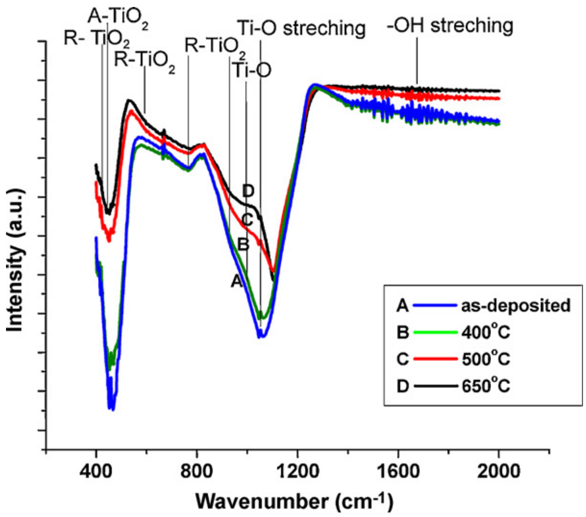

Fig. 11. FTIR spectra of as-deposited and annealed TiO_2 thin films.

765 cm^{-1} and 917 cm^{-1} were attributed to rutile phase of TiO_2 while peak at 990 cm^{-1} corresponds to TiO [21–23]. The peak at 1052 cm^{-1} was attributed to Ti–O bond stretching while broad peak centered around 1622 cm^{-1} is attributed to–OH bond stretching [23,24] responsible for hydrophilic nature of TiO_2 thin films. The decrease in –OH peak intensity at high temperatures of annealing is due to water desorption from TiO_2 films upon annealing. This behavior of TiO_2 films is also in accordance with hydrophobic nature of the films as discussed above.

FWHM of TiO_2 and Ti–O peaks decreased with increased annealing temperature. This can be attributed to increased crystalline structure and increased grain size at higher annealing temperature.

4. Conclusion

We have reported pulsed laser deposition of TiO_2 thin films on glass substrates in O_2 ambient using highly pure rutile grade TiO_2 pellets. Increase in crystalline structure and change in phase from anatase to rutile of TiO_2 films with annealing temperature is reported. Post-annealed TiO_2 films showed the tubular surface morphology. Higher O_2 pressure during deposition helps in improving the crystalline nature of the films. The PL spectra of TiO_2 films showed red shift with increase in annealing temperature with peak position at 3.03 eV for as-deposited film to 3.26 eV for 650 °C annealed film. The UV–vis transmittance spectra showed decrease in transmittance of TiO_2 films with annealing temperature while reflectance spectra showed increase in reflectance with annealing temperature. TiO_2 thin films having as low as 10% reflectance was deposited which is suitable for anti-reflection coating applications. FTIR spectrum showed decrease in FWHM of TiO_2 and Ti–O peaks due to increase in crystalline behavior and increase in grain size upon annealing. The contact angle measurement confirms the higher hydrophobicity of TiO_2 thin films with the annealing temperature. The above results confirm the precise control on the quality of pulsed laser deposited thin films of TiO_2 with different deposition and annealing conditions.

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References

[1] B.S. Richards, J.E. Cotter, C.B. Honsberg, Appl. Phys. Lett. 80 (2002) 1123–1125.
[2] A.R. Armstrong, G. Armstrong, J. Canales, R. Garcia, P.G. Bruce, Adv. Mater. 17 (2005) 862–865.
[3] T. Watanabe, A. Nakajima, R. Wang, M. Minabe, S. Koizumi, A. Fujishima, K. Hashimoto, Thin Solid Films 351 (1999) 260–263.
[4] S. Eliahou-Niv, R. Dahan, G. Golan, Microelectron. J. 37 (2006) 302–307.
[5] K. Bange, C.R. Ottermann, O. Anderson, U.J.U. Jeschkowski, M. Laube, R. Feile, Thin Solid Films 197 (1991) 279–285.
[6] Y. Shuichi, S. Mitsuaki, O. Hajime, O. Hiromichi, Y. Yoshiki, A. Nakao, Jpn. J. Appl. Phys. 46 (2007) 2309–2311.
[7] D.J. Won, C.H. Wang, H.K. Jang, D.J. Choi, Appl. Phys. A 73 (2001) 595–600.
[8] P.I. Gouma, P.K. Dutta, M.J. Mills, Nanostruct. Mater. 11 (1999) 1231–1237.
[9] J.H. Kim, S. Lee, H.S. Im, Appl. Surf. Sci. 151 (1999) 6–16.
[10] S. Yamamoto, T. Sumita, Sugiharuto, A. Miyashita, H. Naramoto, Thin Solid Films 401 (2001) 88–93.
[11] J.M. Lackner, W. Waldhauser, R. Ebner, B. Major, T. Schoberl, Surf. Coat. Technol. 180 (2004) 585–590.
[12] S. Kitazawa, Y. Choi, S. Yamamoto, Vacuum 74 (2004) 637–642.
[13] T. Nakamura, T. Ichitsubo, E. Matsubara, A. Muramatsu, N. Sato, H. Takahashi, Acta Mater. 53 (2005) 323–329.
[14] D. Luca, D. Macovel, C.M. Teodorescu, Surf. Sci. 600 (2006) 4342–4346.
[15] J.D. Deloach, G. Scarel, C.R. Aita, J. Appl. Phys. 85 (1999) 2377–2384.
[16] Y. Xin, K. Han, P.A. Stampe, R.J. Kennedy, J. Cryst. Growth 290 (2006) 459–465.
[17] H. Long, G. Hwang, A. Chen, Y. Li, P. Lu, Thin Solid Films 517 (2008) 745–749.
[18] N. Daude, C. Gout, C. Jouanin, Phys. Rev. B 15 (1977) 3229–3235.
[19] H. Tang, K. Prasad, R. Sanjines, P.E. Schmid, F. Levy, J. Appl. Phys. 75 (1994) 2042–2047.
[20] P. Zeman, S. Takabayashi, J. Vac. Sci. Technol. A 20 (2002) 388–393.
[21] G.V. Chertihin, L. Andrews, J. Phys. Chem. 99 (1995) 6356–6366.
[22] L. Shao, L. Zhang, M. Chen, H. Lu, M. Zhou, Chem. Phys. Lett. 343 (2001) 178–184.
[23] V.G. Erkov, S.F. Devyatoba, E.L. Molodstova, T.V. Malsteva, U.A. Yanovskii, Appl. Surf. Sci. 166 (2000) 51–56.
[24] N.T. McDevitt, W.L. Ban, Spectrochim. Acta 20 (1964) 799–808.