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Surface chemistry and optical property of TiO_2 thin films treated by low-pressure plasma

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Abstract

The low temperature RF plasma treatment was used to control the surface chemistry and optical property of TiO_2 thin films deposited by RF magnetron sputtering with a very good uniformity at 300 °C substrate heating temperature. The XRD pattern indicates the crystalline structure of the film could be associated to amorphous structure of TiO_2 in thin film. The plasma treatment of TiO_2 film can increase the proportion of Ti^{3+} in Ti2*p* and decrease in carbon atoms as alcohol/ether group in C1*s* at the surface. The optical transmittance of the film was enhanced by 50% after the plasma treatment. The surface structure and morphology remain the same for untreated and low-pressure plasma-treated films. Therefore, increase in the optical transmission could be due to change in surface chemistry and surface cleaning by plasma treatment.
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Keywords: Optical property; Thin film; TiO_2; Surface states; Plasma treatment

1. Introduction

TiO_2 films have several advantages for applications in coatings on eye-glasses, glass sheets, flat panel displays and different optical systems [1–3]. The other applications of TiO_2 are in solar cells [4] and very commonly used as a photocatalyst for degradation of environmental pollutants [5,6]. Recent interest is to increase the photoactivity of TiO_2 under visible light region by ion implantation, doping with metals, electron beam and plasma treatment [7–11]. The modification of TiO_2 surface states can increase the photoactivity due to increase in Ti^{3+} surface states of modified TiO_2 [6,12].

The TiO_2 thin films with good optical properties can be deposited by controlling the deposition conditions such as gas flow, ratio of gases mixture, substrate heating, etc., in magnetron sputter systems. In this study, the films were deposited using RF magnetron sputter system and low-pressure plasma treatment was applied to control the surface states (such as Ti^{3+}) and improving optical property of the films. In addition the effects of low-energy plasma treatment on different functionalities associated with carbon (such as C(=O)O*X*, C=O and C–O*X*) at the surface have been also studied.

2. Experimental

RF magnetron sputter system with a titanium target (99.9% purity) was used to deposit TiO_2 films on glass substrates at 300 °C substrate heating temperature. In the deposition system first a base pressure ($\sim 10^{-6}$ Torr) was achieved and argon and oxygen gases were introduced into the chamber at flow rates 40 and 2 standard cubic centimetres per minute (sccm), respectively. The films were deposited at 3 mTorr pressure and 200 W RF power. The TiO_2 film were exposed to the atmosphere for 24 h before the low-pressure plasma treatment was carried out in a two-stage plasma discharge similar to that used in our previous studies [13,14]. A detailed description of operation

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and working principle of this type of reactor has been discussed elsewhere [15–18].

The argon gas plasma was used for the surface modification of TiO_2 films. The substrate was positioned at 75 mm from the grid in the process chamber. The plasma exposure time to TiO_2 films and operating pressure were fixed at 10 min and 20 mTorr, respectively. Dhayal et al. [15] measured the plasma density and electron temperature at different values of grid bias voltage, distance form the grid and RF power in this type of discharge. It was reported that when the grid was biased <5 V, electron temperature remains approximately constant <0.5 eV ($E_i<3$ eV). Therefore, in this current set-up (similar to [15]) approximately constant argon ion energy (<3 eV) was used for TiO_2 films surface modification at different RF powers.

The surface structure characterization of the plasma modified TiO_2 film was carried out by obtaining XRD (model D/MAX1200 (Rigaku, Geiger) at 40 kV, 20 mA using a Cu target) spectrum. X-ray photoelectron spectroscopy (XPS) was performed with a VG-Scientific ESCALAB 250 spectrometer with monochromatized Al$K\alpha$ X-ray source at Korea Basic Science Institute. Computer-aided surface analysis for XPS has been used to curve fit the narrow scans XPS spectrums. The electron exit angle was set normal to the substrate. Multimode SPM with nanoscoe III controller (Digital instrument, USA) in tapping mode instrument was used for atomic force microscopy (AFM) measurements at Chonnam National University, Korea. Transmission spectra were recorded from 300 to 800 nm range with SHIMADZU UV-3101 PC UV–Vis spectrophotometer at normal incidence.

3. Results and discussion

The crystalline structure of the film was observed by XRD patterns for both plasma treated and untreated samples and shown in Fig. 1. There were no sharp diffraction lines and it looks quite similar to the XRD pattern observed by Abdel Aziz et al. [19]. In this study, the films were deposited at 300 °C substrate heating temperature and the main peak of TiO_2 anatase structure (2ϑ values) appears around at 24.5–25 whereas it should be positioned at 25.3 for TiO_2 anatase structure. Therefore, the broad-hump indicates the amorphous structure of the film and glass substrate. The peak position can be affected by substrate, e.g. both TiO_2 and substrate combines together, and overlapped. Madhusudan Reddy et al. [20] had studied the effects of temperature on structure of TiO_2 and the amorphous anatase transformation was complete in the temperature range 400–600 °C. The XRD peaks of TiO_2 calcined at 300 °C are weak in comparison to those of the samples calcined at higher temperatures. This suggests that a significant amount of amorphous phase still remains at the surface similar to our observations. The interesting thing that can be noted is that there is no change in the structure due to plasma surface modification.

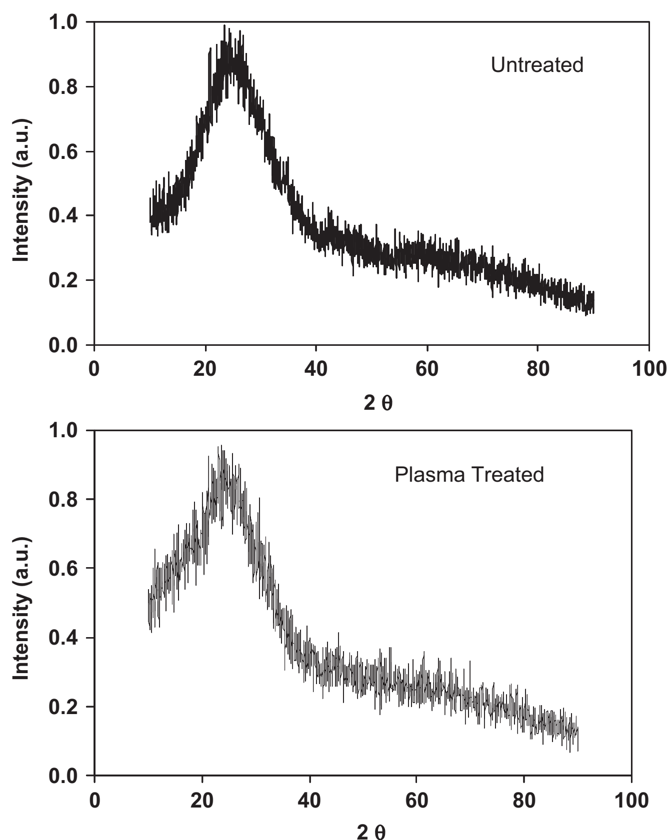

Fig. 1. XRD pattern of untreated and plasma-treated TiO_2 film.

To obtain the surface morphology, atomic force microscopic measurements were carried out. Fig. 2 shows AFM observation of untreated and 20 W RF plasma-treated TiO_2 thin films. The surface roughness of TiO_2 films was <10 nm and no significant changes were observed due to plasma treatment in the surface morphology.

The deposition rate was kept constant and film thickness was calculated. All the films were deposited with the similar conditions and had same thickness (about 160 nm). Fig. 3 shows optical transmittance of untreated and plasma-treated TiO_2 films at three different RF powers. About 50% increase in the optical transmittance of films was observed after plasma treatment. The details of surface chemistry also need to be looked into to have a better correlation between optical transmittance of the films and surface chemistry.

The quantitative elemental analysis of % of atomic proportion as Ti, O and C atoms at film surface with different RF powers is shown in Fig. 4. The oxygen elemental proportion at the surface remained approximately constant for plasma treated and untreated films. A small increase in the % of proportion of carbon atoms at the surface was observed with increasing RF powers. The increase in % of carbon atoms at the surface might be coming from the

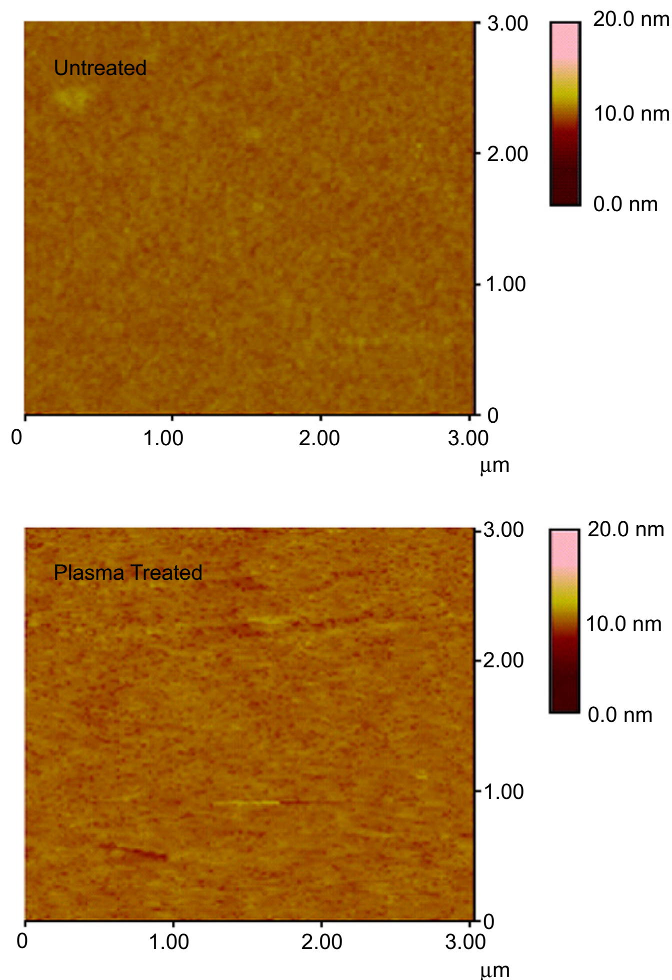

Fig. 2. AFM picture of untreated and plasma-treated TiO_2 film.

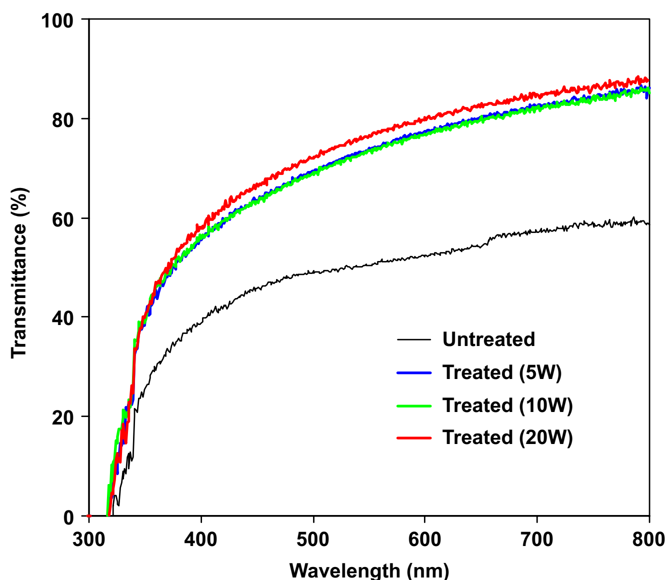

Fig. 3. Transmittance spectra of plasma treated and untreated TiO_2 films.

impurities that exist in the chamber (at the base pressure of 10^{-5} Torr many impurities can exist in the chamber and those can influence the surface chemistry [21]).

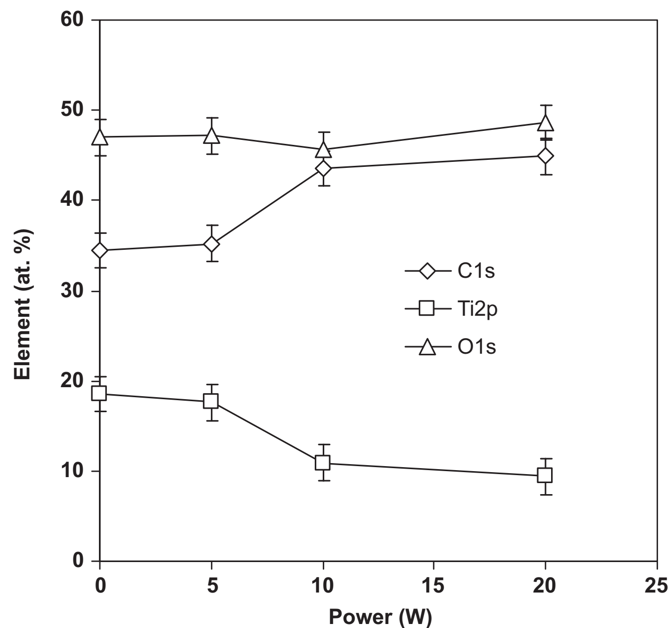

Fig. 4. Atomic proportion (%) as Ti, O and C in XPS wide scan spectra of TiO_2 films with RF powers. (Zero power result is associated with untreated film.)

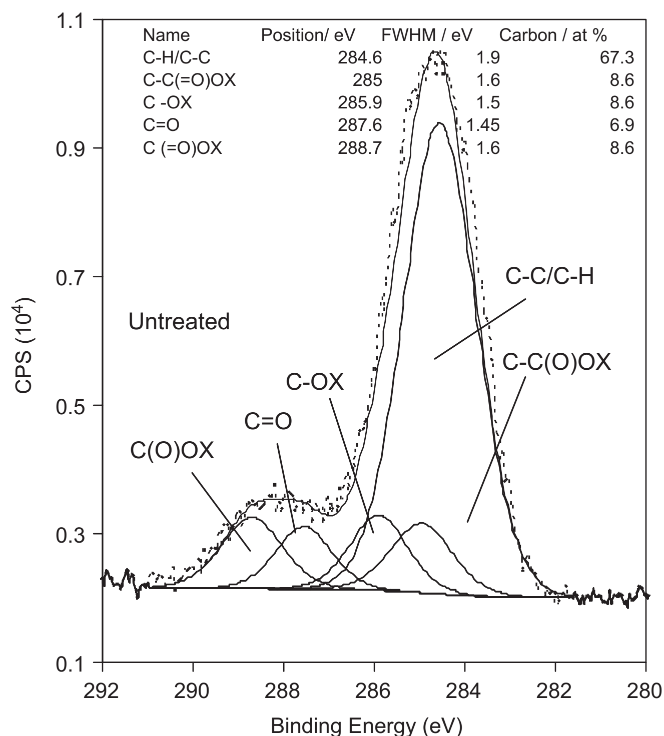

Fig. 5. Narrow scan XPS C1*s* peak fitted spectrum of untreated TiO_2 film.

Fig. 5 shows high-resolution C1*s* XPS spectra for untreated TiO_2 films. In the C1*s* spectra the position of C–H/C–H was adjusted to 284.6 eV and other peak of different carbon environments were fixed relative to this peak [22]. The C1*s* spectrums for untreated film surface was

fitted with five peaks as; hydrocarbon (C–H/C–C) at 284.6 eV, C–C(=O)OX at 285.0 eV, alcohol/ether (C–OX) at 285.9 eV, carbonyl (C=O) at 287.6 eV, and carboxylic/ester (C(=O)OX) at 288.7 eV. Fig. 6 shows high-resolution C1s XPS spectra for plasma treated (at 20 W RF power) TiO_2 films. In case of plasma-treated thin film, a shift of 0.9 eV towards to the higher binding energy was observed in the narrow scan C1s spectrum. This was adjusted to carbon peak (C–C/C–H at 284.6 eV) and same five peaks were fitted as; C–H/C–C at 284.6 eV, C–C(=O)OX at 285 eV, C–OX at 286.0 eV, C=O at 287.4 eV, and C(=O)OX at 288.7 eV.

The analysis of change in different titanium surface states was also carried out. The narrow scan Ti2p XPS spectrums of untreated and plasma-treated (at 20 W RF power) TiO_2 thin films are shown in Fig. 7 and 8. The spectrum of untreated film was fitted with four peaks as $Ti^{3+}2p_{3/2}$ at 454.6 eV, $Ti^{4+}2p_{3/2}$ at 455.8 eV, $Ti^{3+}2p_{1/2}$ at 458.7 and $Ti^{4+}2p_{1/2}$ 461.4. The Ti2p XPS spectrum of 20 W RF plasma-treated thin film surface was also fitted with four peaks as $Ti^{3+}2p_{3/2}$ at 455.0 eV, $Ti^{4+}2p_{3/2}$ at 456.6 eV, $Ti^{3+}2p_{1/2}$ at 460.2 eV, and $Ti^{4+}2p_{1/2}$ 462.2 eV. For the plasma modified Ti2p peak fitting the area of $Ti^{3+}2p_{1/2}$ was fixed at $0.5 \times$ the area of $Ti^{3+}2p_{3/2}$ due to the 3 1/2 and 1/2 spin states [22].

To have detailed analysis of different oxygen atomic states at the surface, a narrow scan O1s XPS spectrum was obtained. Fig. 9 shows peak fitted O1s narrow scan XPS spectrums for both untreated and 20 W plasma-treated

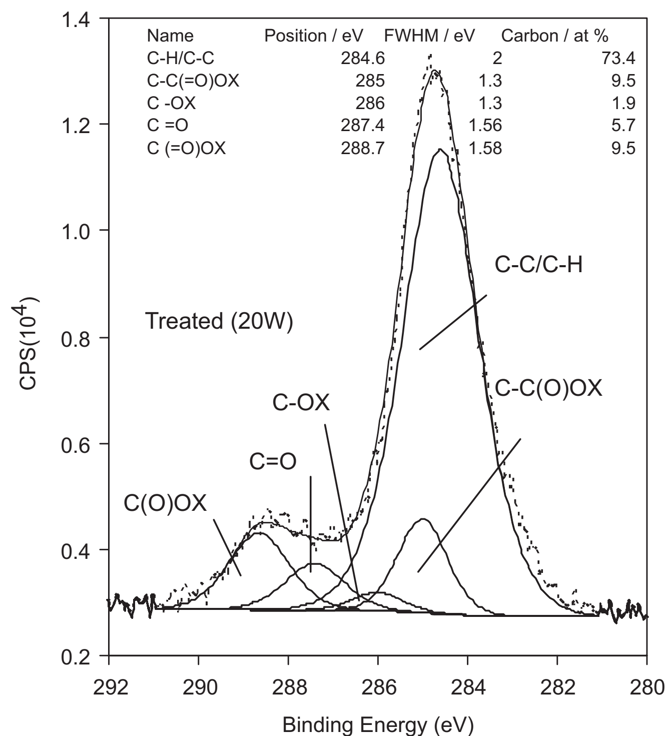

Fig. 6. Narrow scan XPS C1s peak fitted spectrum of 20 W RF power plasma-treated TiO_2 films.

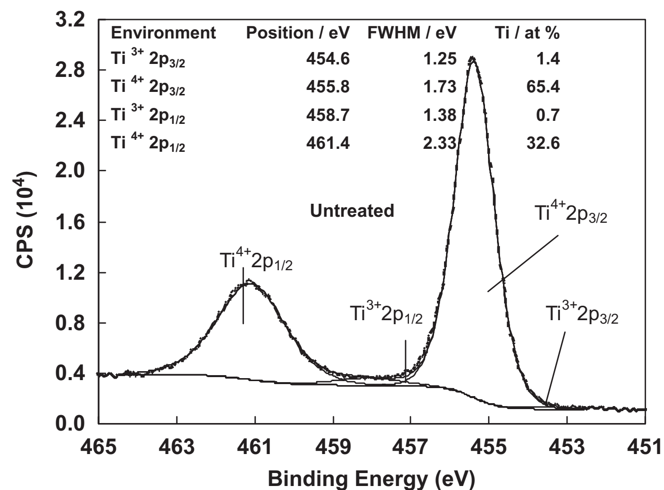

Fig. 7. Narrow scan XPS Ti2p peak fitted spectrum of untreated TiO_2 film.

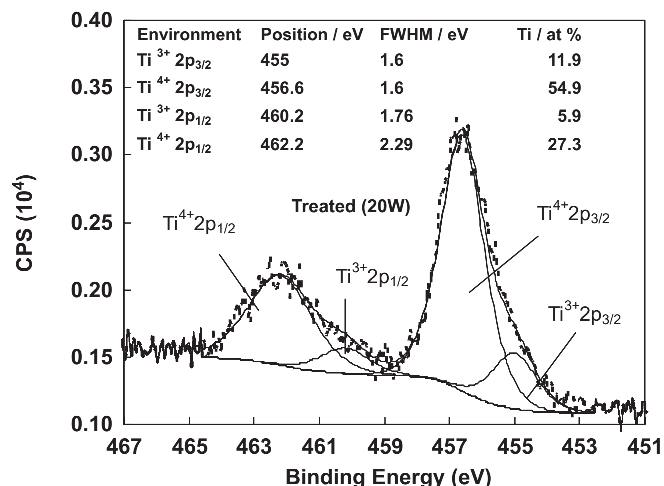

Fig. 8. Narrow scan XPS Ti2p peak fitted spectrum of 20 W RF power plasma-treated TiO_2 films.

TiO_2 thin film surface. The spectrums were fitted with three peaks and the chemical shift relative to the first peak is quoted in parenthesis. The peaks in untreated film were [TiO_2] at 526.8 eV (0 eV), [Ti_2O_3/hydroxide functionality] at 527.9 eV (1.1 eV), and [TiO(H/C)Ti] at 529.1 (2.3 eV) [9]. For plasma-treated thin films, again, three peaks were fitted as TiO_2 at 527 eV (0 eV), Ti_2O_3 at 528.2 eV (1.2 eV), and [TiO(H/C)Ti] at 529.3 (2.3 eV).

The quantitative variation of Ti^{4+} to Ti^{3+} surface states in Ti2p with different powers is shown in Fig. 10. The results showed about 18% decrease in Ti^{4+} after plasma treatment of the films at 20 W RF power and this was converted into Ti^{3+} surface states. Therefore, the Ti^{3+} surface states on the titanium oxide films surface can be controlled by plasma treatment of the films.

The quantitative variation of different functionalities of carbon environment at the surface of the film is shown in

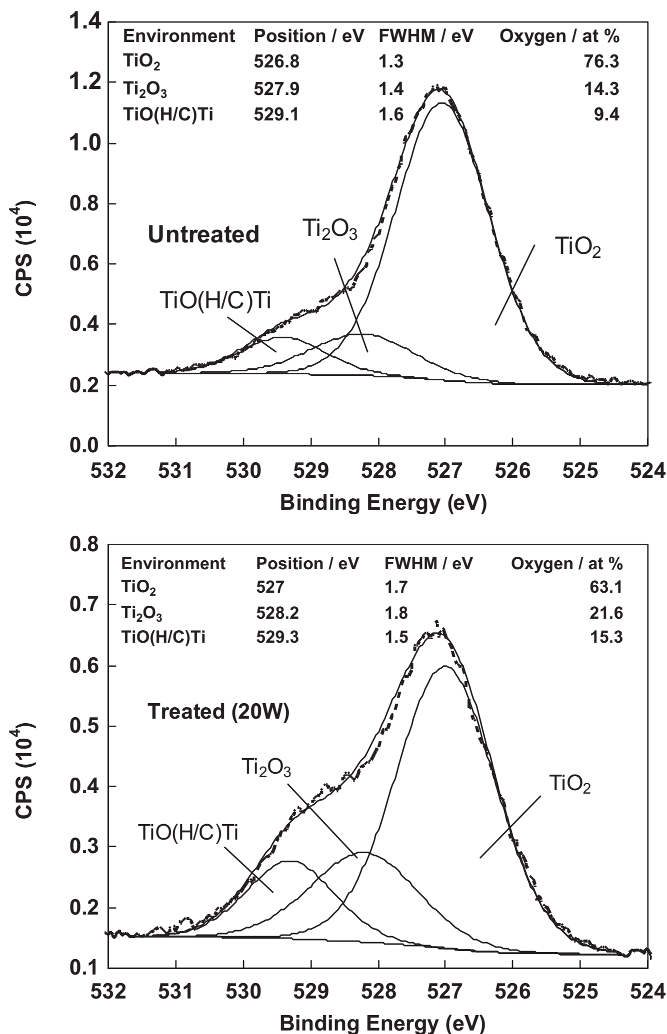

Fig. 9. Narrow scan XPS O1*s* peak fitted spectrum of untreated and 20 W RF power plasma-treated TiO_2 films.

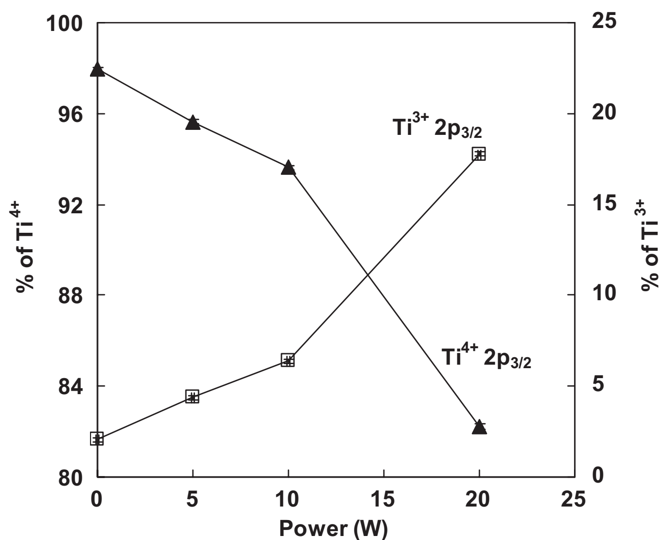

Fig. 10. Proportion of different oxidation states of titanium (%) in Ti2*p* with RF powers.

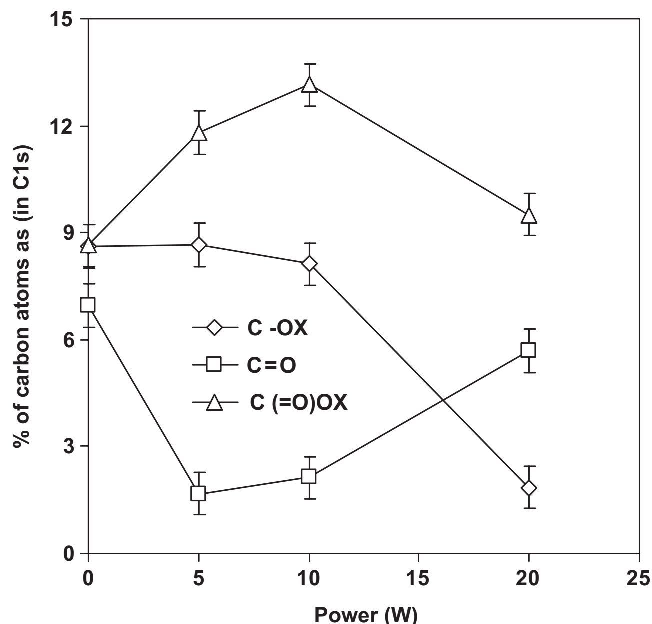

Fig. 11. Proportion of carbon atoms (%) as alcohol/ether (C–O*X*), carbonyl (C=O), carboxylic/ester (C(=O)O*X*) in C1*s* with RF powers.

Fig. 11 with a different RF power plasma treatment. The result shows a significant decrease in the proportion of carbon atoms as alcohol/ether (C–O*X*) and carbonyl (C=O) functionality whereas an increase in the carbon atoms as (C(=O)O*X*)) functionality was observed with increasing RF power. The control of these functional groups is useful to increase the biological performance of these films for implantable devices whereas the increase in Ti^{3+} surface sates is useful to enhance the photocatalytic activities of these films.

There are several methods to control the optical properties of TiO_2 thin films and they include, controlling the deposition parameters and doping with different materials. Gracia et al. [23] had studied the optical, microstructural, and structural properties of TiO_2 thin films prepared by ion beam-induced and plasma-enhanced chemical vapor deposition at different temperatures. It has been reported that nonstoichiometric thin films with a high concentration of Ti^{3+} centers can be prepared and associated optical properties of the films can be observed. It was concluded that the anatase structure with a higher porosity has advantages in favoring the photoefficiency of the system. Wang et al. [24] had reported the optical properties of anatase TiO thin films prepared by aqueous sol–gel process at low temperature. Recently, Ghodsi et al. [25] had studied the influence of pH on the optical and structural properties of spin-coated TiO_2 thin films. The low-pressure low-energy (<5 eV) ion plasma treatment does not change the surface structure and roughness. Hence the change in optical properties can directly be associated with the relevant change in the surface chemistry of the films. The other

advantage on this process is in surface cleaning and possibility that can also contribute to the enhancement of optical properties.

4. Conclusion

The surface chemistry and surface states of TiO_2 thin films can be controlled by low-energy ($<3\,eV$) argon ions treatment of the films. The crystalline structure of the film could be associated to amorphous structure of TiO_2 in thin film. The plasma treatment of TiO_2 film can increase the proportion of Ti^{3+} in Ti2*p* and decrease carbon atoms as alcohol/ether group in C1*s* at the surface. The optical transmittance of the film was enhanced by 50% after the plasma treatment. The surface structure and morphology remains same for untreated and low-pressure plasma-treated films. Therefore the increase in the optical transmission could be due to change in surface chemistry and surface cleaning by plasma treatment.

Acknowledgments

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References

[1] M. Gioti, S. Logothetidis, C. Charitidis, Y. Panayiotatos, I. Varsano, Sensors Actuators A 99 (2002) 35.
[2] R. Pareek, A.S. Joshi, P.D. Gupta, P.K. Biswas, S. Das, Opt. Laser Technol. 37 (2005) 369.
[3] J. Szczyrbowski, G. Brauer, G. Teschner, A. Zmelty, Surf. Coat. Technol. 98 (1998) 1460.
[4] G.S. Vicente, A. Morales, M.T. Gutierrez, Thin Solid Films 403–404 (2002) 335.
[5] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[6] J. Jun, M. Dhayal, J.H. Shin, J.C. Kim, N. Getoff, Radiat. Phys. Chem. 75 (5) (2006) 583.
[7] J. Jun, J.H. Shin, M. Dhayal, Appl. Surf. Sci. 252 (10) (2005) 3871.
[8] B. ORegan, M. Gratzel, Nature 353 (1991) 737.
[9] J.M. Herrmann, J. Disdier, P. Pichat, Chem. Phys. Lett. 108 (1984) 618.
[10] H. Yamashita, M. Harada, J. Misaka, H. Nakao, M. Takeuchi, M. Anpo, Nucl. Instrum. Meth. Phys. Res. B 206 (2003) 889.
[11] J. Jun, J.H. Shin, J.S. Choi, M. Dhayal, J. Biomed. Nanotechnol. 2 (2006) 152.
[12] M. Anpo, M. Takeuchi, J. Catal. 216 (2003) 505.
[13] M. Dhayal, H.G. Jeong, J.S. Choi, Appl. Surf. Sci. 252 (5) (2005) 1710.
[14] M. Dhayal, Su-In Cho, Vacuum 80 (6) (2005) 636.
[15] M. Dhayal, D. Forder, R.D. Short, D. Barton, J.W. Bradley, Surf. Coat. Technol. 162 (2–3) (2003) 294.
[16] M. Dhayal, J.W. Bradley, Surf. Coat. Technol. 184 (1) (2004) 116.
[17] M. Dhayal, D. Forder, R.D. Short, J.W. Bradley, Vacuum 70 (1) (2003) 67.
[18] M. Dhayal, K.L. Parry, R.D. Short, J.W. Bradley, J. Phys. Chem. B 108 (37) (2004) 14000.
[19] M.M. Abdel-Aziz, I.S. Yahia, L.A. Wahab, M. Fadel, M.A. Afifi, Appl. Surf. Sci. 252 (2006) 8163.
[20] K. Madhusudan Reddy, C.V. Gopal Reddy, S.V. Manorama, J. Solid State Chem. 158 (2001) 180.
[21] M. Dhayal, M.R. Alexander, J.W. Bradley, Appl. Surf. Sci. 252 (22) (2006) 7957.
[22] G. Beamson, D. Briggs, High Resolution XPS of Organic Polymers—The Scienta ESCA300 Database, Wiley, Chichester, 1992.
[23] F. Gracia, J.P. Holgado, A.R. Gonzalez-Elipe, Langmuir 20 (2004) 1688.
[24] Z. Wang, U. Helmersson, P.O. Kall, Thin Solid Films 405 (2002) 50.
[25] F.E. Ghodsi, F.Z. Tepehan, G.G. Tepehan, Surf. Sci. (2007), in press.